SYSTEM ANALYSIS OF GELLED SPACE-STORABLE PROPELLANTS

Contract NAS 7-473, SA-3

Prepared for

OFFICE OF ADVANCED RESEARCH AND TECHNOLOGY
National Aeronautics and Space Administration
Washington, D.C.

Final Report 1038-04F

July 1970

AEROJET LIQUID ROCKET COMPANY
A DIVISION OF AEROJET-GENERAL
SACRAMENTO, CALIFORNIA

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FOREWORD

Contract NAS 7-473, SA-3, "System Analysis of Gelled Space-Storable Propellants," was performed by the Aerojet Liquid Rocket Company at Sacramento, California. This final report describes the accomplishments for the fourth year of the contract, from June 1969 through May 1970.

The fourth year's effort was performed by Engineering Operations, Dr. D. E. Robison, Manager. The Aerojet Program Manager and Project Engineer was Mr. R. H. Globus. The diborane and oxygen difluoride gel formulation and testing studies were performed by Mr. Globus with the assistance of Mr. J. A. Cabeal. Dr. S. D. Rosenberg and Dr. E. M. Vander Wall acted as consultants during this program.

The NASA Project Manager for Contract NAS 7-473, SA-3, was Mr. J. Suddreth, NASA Headquarters, OART; the NASA Technical Manager was Mr. D. L. Young of the Jet Propulsion Laboratory.

SYNOPSIS OF PRIOR WORK

The first phase of this program consisted of an analytical study to establish the effects that the use of gelled, space-storable propellants has on engine systems for spacecraft. The analysis considered passive storability, zero gravity control, expulsion, sloshing, ignition, multiplicity of restarts, propellant utilization, throttlability, performance, heat transfer, and other system design aspects. The results of this study indicated that: (1) gelation raises the frequency at which the slosh modes occur and greatly dampens the slosh modes; (2) the use of gels, because of their structure when at rest may permit the elimination of positive expulsion devices; (3) the use of gelled propellants poses nor major problems with respect to controls; (4) possible advantages are reduced leakage and simplified propellant level sensing as the shape and position of the gel would be known; and (5) the only significant design change required for gel injection with conventional injectors is a requirement to increase pressure drop values by approximately 67% to improve the atomization of the gelled propellant.

Among the disadvantages anticipated with the use of conventional gelling agents for gelation of the propellants in comparison to the neat propellants were: (1) lower specific impulse values; (2) greater residual propellant quantities; (3) impairment of engine restarts by solid residues; and (4) larger transfer lines. To minimize disadvantages resulting from the use of gelled propellants, a new type of gelant was suggested, i.e., extremely small particles of energetic compounds which are volatile at ambient temperatures. The new class of gelants reduces specific impulse losses to a few percent; restart capability is not impaired because the gelants vaporize from the engine manifold during heat soak-back conditions; the particulate gels shear-thin readily, minimizing propellant adherence to walls and increased pressure drop requirements.

Synopsis of Prior Work (cont.)

Initial experimental efforts during the second phase of this program were devoted to the gelation of oxygen difluoride with an energetic, particulate gelant. Liquid oxygen difluoride was gelled with fine particles of solid chlorine trifluoride. The structure index of gelled oxygen difluoride was measured at several gelant concentrations; an excellent gel was obtained at a chlorine trifluoride concentration of 5.5 wt%. The flow properties of gelled oxygen difluoride were measured in a novel flow viscometer; the flow results demonstrated that it would be possible to transfer the gelled propellant in conventionally designed pumps and lines. A measurement of the particle size of the solid chlorine trifluoride using a spectral technique indicated that, over the range of experimental parameters investigated, experimental formulation conditions did not affect the size of the particles. Based on the results obtained on this phase, it was recommended that: (1) the properties of gelled oxygen difluoride be determined in detail; and (2) the gelation of diborane, using the techniques developed on this program, be undertaken.

During the third phase of this program, liquid diborane was gelled with fine particles of trimethylaminoborane and the structure index of the gel was measured at several gelant concentrations; an excellent gel was obtained at a trimethylaminoborane concentration of 10 wt%. The gelled diborane was stored at 210°R for 12 days without any evidence of settling or gel degradation, and the ability to flow gelled diborane was demonstrated.

The storage properties of liquid oxygen difluoride gelled with chlorine-trifluoride particles were measured. In no case did the gel remain stable for longer than eight days. Based on the results obtained during this phase of the program, it was recommended that the properties of gelled diborane be determined in detail and that work be continued to develop a satisfactory gelant for liquid oxygen difluoride during the fourth phase of this program.

ABSTRACT

Liquid oxygen trifluoride was gelled with fine particles of $ClF_3 \cdot BF_3$ and the gel was stored for 30 days at -196°C (139°R). The OF_2 gel was flowed at four different gelant concentrations and at various driving pressures. At higher flow rates, the gels shear-thinned to a point that their flow behavior approached that of water. Bromine trifluoride, bromine pentafluoride and boron trifluoride were evaluated as gelants for OF_2. In no case was a satisfactory gel obtained.

Liquid diborane was gelled with fine particles of $(CH_3)_3N \cdot BF_3$ and the gel was stored for 30 days at -156°C (210°R). The diborane gel was flowed at 5 different gelant concentrations and at various pressure drops. At higher flow rates, the gels shear-thinned to a point that their apparent viscosity was less than that of water at the same shear rate. Liquid diborane was gelled with fine particles of $(CH_3)_3N \cdot BH_3$. The storage stability of this gel did not meet program objectives.

As the structure of the gelled OF_2 and gelled B_2H_6 increased, the apparent viscosity of the gels increased at a particular shear rate. However, because of the extreme shear-thinning that occurred when the gels were flowed, no quantitative correlation between the apparent viscosity of the gel and the structure of the gel when at rest could be developed.

Gelled OF_2 and gelled B_2H_6 do not core or cling to vessel walls while the gels are flowed; propellant acquisition and utilization will not be hampered by gelation. The flow behavior of particulate gels is discussed and the effect of gelation on propellant system performance has been determined.

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SECTION I

INTRODUCTION

1. OBJECTIVE

The objective of this study was to complete the physical characterization of gelled oxygen difluoride (OF_2) and gelled diborane (B_2H_6). After the accomplishment of this objective, the gel behavior during expulsion was measured. In addition, the flow data obtained during this work was reviewed to determine if a correlation existed between flow properties and degree of gel structure. As the structure of the gelled OF_2 and gelled B_2H_6 increased, the apparent viscosity of the gels increased at a particular shear rate. However, because of the extreme shear-thinning that occurs when the gels are being flowed, no quantitative correlation between the apparent viscosity of the gel and the structure of the gel when at rest could be developed. Therefore, a preliminary investigation was conducted to determine the feasibility of measuring the degree of structure of a gel at rest with a technique that did not require manual manipulation.

2. ADVANTAGES OF GELATION

Gelled propellants offer the following improvements in rocket system performance: (1) positional stability in a zero-g environment, and (2) reduced sloshing. These advantages are of considerable importance when propellant systems are being considered for deep space missions. The disadvantages of gelled propellants are: (1) a reduction in performance; and (2) an impairment in restart capability if an inert, high-melting, particulate material is used as the gelling agent. However, by the proper selection of gelling agents, performance losses can be reduced to a point that they are no longer significant and impairment of restart capability can be eliminated.

The structure a gel possesses when at rest gives the material the properties of a coherent semi-solid. Consequently, until a shear force is

I, 2, Advantages of Gelation (cont.)

applied, the material will remain in its original position. This property of positional stability which is imparted to a liquid by gelation offers an important advantage to liquid propellants being considered for deep-space applications. It eliminates the need for a positive expulsion device, with its complexity and, in the case of fluorine-containing oxidizers, serious material problems, to ensure that the propellant will be delivered to the engine.

The reduction of sloshing caused by gelling a propellant was demonstrated by Aerojet under Contract NAS 7-473 (Reference 1). It was experimentally demonstrated that: (1) the resonant frequency for gels occurred at higher values than for ungelled liquid; and (2) the motion decayed in two cycles or less in gelled systems compared to 30 to 40 cycles for ungelled liquids.

3. PARTICULATE GELANTS

Two classes of gels are known. The first is formed by a reaction or interaction between the gelling agent and the liquid being gelled. This type of gelling agent is polymeric (high molecular weight) or becomes polymeric during gel formation. Polymeric gels cannot be used with OF_2 because all known polymeric gels would be reactive. Polymeric gels would not be satisfactory for use with diborane because they would be nonvolatile and would leave a residue in the propellant lines.

The second class of gel is a "particulate gel". Apparently there are two types of particulate gels. The first type of particulate gel occurs when the gelation of the liquid arises only because of the surface properties of the particles. This occurs when the particles are small enough so that there is an attraction between the individual particles which causes them to form interconnecting chains or networks which trap the liquid. A gel-like material

I, 3, Particulate Gelants (cont.)

is the result. The property that makes the first type of particulate gel distinctive is the fact that gel formation is essentially independent of the chemical properties of the liquid. In other words, if the particles are small enough so that these chains or networks form, the particles will gel any liquid in which they are insoluble and nonreactive. This independence of liquid properties is demonstrated by the fact that the volume of gelling agent required to achieve a given degree of gel structure remains remarkably constant from liquid to liquid.

The second type of particulate gel occurs when, in part, the gelation of the liquid arises because of an interaction between the particles and the liquid analogous to the formation of a hydrogen bond. When this interaction between the particles and liquid occurs, gelation of the liquid is due both to the surface properties of the particle and the attraction caused by chemical bonding, i.e., an interaction between the liquid and the particle. With this second type of particulate gel, a given volume concentration of gelant will provide a stiffer gel with a liquid.

If the material from which the particles are prepared is volatile in the correct temperature range, the particles will vaporize along with the propellant during an in-space coast-sequence, thereby eliminating the formation of a residue of solid materials in propellant lines and assuring the same restart capability as ungelled liquids.

Oxygen difluoride, gelled under Contract NAS 7-473, SA-1, with particles of ClF_3, and diborane, gelled under Contract NAS 7-473, SA-2, with particles of $(CH_3)_3N \cdot BH_3$, are particulate gels of the first type where there does not appear to be any interaction between the liquid and the particles. Oxygen difluoride, gelled under Contract NAS 7-473, SA-3, with particles of $ClF_3 \cdot BF_3$, and diborane, gelled under Contract NAS 7-473, SA-3 with particles of

I, 3, Particulate Gelants (cont.)

$(CH_3)_3N \cdot BF_3$, are particulate gels of the second type where there is an apparent interaction between the particles and the liquid.

The remainder of this report deals with the experimental efforts conducted to complete the physical characterization of gelled oxygen difluoride and diborane which were developed under Contract NAS 7-473, SA-1 and SA-2.

SECTION II

SUMMARY

The technical effort on this program was divided into four tasks. The work performed and the results and their significance are summarized below, as are recommendations for future work.

Liquid oxygen difluoride was gelled with fine particles of the chlorine trifluoride·boron trifluoride adduct. Three batches of gelled oxidizer, totaling 2300 cc (9.0 lb), were prepared. In addition, volatility of the gelling agent at 25°C was conclusively demonstrated.

The chlorine trifluoride·boron trifluoride adduct particles were prepared by reacting chlorine trifluoride with boron trifluoride in evacuated tanks, diluting the gaseous adduct with helium, and injecting the gaseous mixture beneath the surface of liquid nitrogen. Oxygen difluoride was added to the mixture and the nitrogen sparged off with a stream of helium. After dispersion of the particles in oxygen difluoride, a stable gel formed. The chlorine trifluoride·boron trifluoride particles also gelled liquid nitrogen.

The gelled oxygen difluoride was stored at -196°C (139°R) for 30 days without any evidence of particle settling or gel degradation. The oxygen difluoride gels were flowed at four different gelant concentrations and at various pressure drops between 2.0 and 9.0 psi. At higher flow rates, the gels shear-thinned to a point that their flow behavior approached that of water. The gels were flowed in the turbulent region.

Other gelling agents evaluated for use with oxygen difluoride were bromine pentafluoride, bromine trifluoride, and boron trifluoride. In no case was a satisfactory gel obtained with these candidate gelants.

Liquid diborane was gelled with fine particles of the trimethylamino·boron trifluoride adduct. Four batches of gelled fuel, totaling 3490 cc (3.6 lb),

II, Summary (cont.)

were prepared. In addition, the volatility of the gelling agent under engine shutdown conditions was conclusively demonstrated.

The trimethylamino·boron trifluoride adduct particles were prepared by reacting trimethylamine dissolved in liquid methane with boron trifluoride. Diborane was added to the mixture and the methane was sparged off with a stream of helium. After dispersion of the particles in diborane, a stable gel formed. The trimethylamino·boron trifluoride particles also gelled liquid methane.

The gelled diborane was stored for 30 days at -156°C (210°R). The gel showed no evidence of deterioration. Additional testing showed that the gel was stable with respect to exudate formation to temperatures as high as -131°C (255°R). The diborane gels were flowed at five different gelant concentrations and at various pressure drops. At higher flow rates, the gels shear-thinned to the point that their apparent viscosity was less than that of water at the same shear rate.

Trimethylaminoborane was evaluated as a gelant for diborane. While this gelant provided excellent gels, the gel storage stability did not meet program objectives.

The flow data obtained with gelled oxygen difluoride and diborane were reviewed to determine if a useful correlation exists between flow properties and gel structure. A correlation between apparent viscosity and gel structure does exist. However, because of the extreme shear-thinning that occurs, it was not possible to develop a useful relationship. Consequently, a novel procedure was developed which does not require manual manipulation for measuring the structure of particulate gelled propellants. A soft iron rod, having a disc on the lower end, is immersed in the gel. A magnetic field, created by a hollow core electromagnet, is increased in stepwise increments until the

II, Summary (cont.)

rod moves. The voltage required to create a magnetic field strong enough to start the movement of the iron rod provides a measure of gel structure.

The behavior of the gels in regard to hang-up and coring was observed during the course of the flow measurements. There was no evidence of the gels coring at any driving pressure and the walls drained clean as the gel level decreased. Consequently, it is concluded that propellant acquisition and utilization will not be hampered by gelation.

The specific impulse penalty caused by gelation of OF_2 is 2.5% and the performance penalty caused by the gelation of diborane is 0.8%. The specific impulse penalty incurred by the gelant concentrations required for both propellants is 3.2%, thereby reducing the theoretical performance from 372 sec to 360 sec at P_c/P_e = 1000/14.7 psia and ε = 40:1.

Based on the results obtained on this program it is recommended that: (1) the performance of the gelled OF_2/gelled diborane bipropellant combination be evaluated at the 100-lb thrust level; and (2) long-term storage tests (6 to 12 months) of the gelled propellants be started. Concurrently with the performance tests, propellant acquisition techniques and overall gel behavior should be further evaluated.

SECTION III

TECHNICAL DISCUSSION

This study was a continuation of Contract NAS 7-473 and Supplemental Agreements 1 and 2, System Analysis of Space-Storable Propellants, which consisted of sixteen tasks: Task I--Preliminary Investigations; Task II--Preliminary Analysis; Task III--Component Design Analysis; Task IV--System Design Analysis; Task V--Documentation; Task VI--Comprehensive Review; Task VII--Development of Techniques To Gel Oxygen Difluoride and To Measure Engineering Properties of the Gel; Task VIII--Gelation of Oxygen Difluoride with Fluorinated Oxidizers; Task IX--Measurement of Engineering Properties of Gelled Oxygen Difluoride; Task X--Documentation; Task XI--Gelled Oxygen Difluoride Storage Tests; Task XII--Characterization of Gelled Oxygen Difluoride Flow Properties; Task XIII--Diborane Literature Survey; Task XIV--Gelation of Diborane; Task XV--Measurement of the Properties of Gelled Diborane; Task XVI--Documentation. This continuation was divided into four technical tasks: Task XVII--Physical Characterization of Gelled Oxygen Difluoride and Diborane; Task XVIII--Correlation of Viscosity and Gel Structure; Task XIX--Expulsion Tests; and Task XX--Documentation. The work performed and the results and their significance are discussed in this section.

1. TASK XVII--PHYSICAL CHARACTERIZATION OF GELLED OF_2 AND B_2H_6

This task was divided into two phases: Phase 1, Gelation of OF_2 with New Gelants, Measurement of Gelled OF_2 Storage Properties and Flow Properties, and Phase 2, Measurement of Gelled B_2H_6 Storage Properties and Flow Properties. The work done under Phase 1 will be discussed first.

a. Phase 1, Gelation of OF_2 with New Gelants and Determination of Gelled OF_2 Storage and Flow Properties

The results of the measurement of the storage properties of gelled OF_2 using ClF_3 particles as the gelant, completed during the last

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

supplement to this contract, demonstrated that this gelled oxidizer formulation may not possess sufficient storage stability to meet the anticipated use-requirements. Consequently, it was decided that no further work with liquid OF_2 gelled with ClF_3 particles would be conducted. However, as the versatility of the general technique for preparing fine particles capable of gelling cryogenic liquids has been amply demonstrated during the course of this study, it was decided that additional work was warranted to find another gelling agent for liquid OF_2.

Two types of materials are available as gelants for OF_2. The first type comprises other interhalogens, such as bromine pentafluoride (BrF_5), etc. While these materials would be analogous to ClF_3 as gelants, their substantially higher melting points and higher molecular weight should tend to decrease their solubility in liquid OF_2. Reduced solubility enhances the possibility of preparing a gel which meets the storage requirements.

The second type of material is an adduct. During the last supplement to this contract, trimethylaminoborane, a classic chemical adduct, was synthesized in liquid methane by reacting trimethylamine with diborane dissolved in liquid methane. Thus, the feasibility of the in-situ synthesis of gelants, i.e., adducts, in a cryogenic liquid was demonstrated. Diborane gelled with trimethylaminoborane demonstrated storage stability at 156°C (210°R) for 12 days, at which time a mechanical failure led to termination of the test. The adducts, being salt-like materials, offer a very attractive group of candidate gelling agents. By selecting the proper adduct, the volatility of the gelling agents can be assured and their salt-like characteristics greatly enhance the possibility that they will be insoluble in the space-storable propellant.

Because the addition of the other interhalogens, such as bromine pentafluoride (BrF_5), etc., appeared to present the fewest experimental

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

problems, the feasibility of using these materials as gelling agents was the first approach evaluated experimentally. However, the experimental work with the adducts will be reported first because this work resulted in the preparation of gelled OF_2 which met the program objectives.

(1) Selected Properties of $ClF_3 \cdot BF_3$

To ensure that the gelling agent selected will not impair restart capability, it is necessary that the gelling agent be volatile under the conditions that exist in a rocket engine immediately after shutdown. Consequently, if information regarding the volatility of a candidate gelling agent was not readily available in the literature, the vapor pressure of the candidate gelant was measured before it was evaluated as a gelant for the propellant. The results of the measurement of the vapor pressure of chlorine trifluoride·boron trifluoride/adduct ($ClF_3 \cdot BF_3$) are presented below.

Experiment 77*

Equal molar quantities of BF_3 and ClF_3 vapor were mixed in a steel vessel and the vapor pressure of the adduct that formed was measured. The results of the vapor pressure measurement are presented in Table I.

TABLE I

VAPOR PRESSURE OF $ClF_3 \cdot BF_3$ ADDUCT

Temperature °C	Vapor Pressure mm Hg	Calculated Pressure Assuming No Adduct Formation mm Hg
21	1091	1124
0	393	938
-78.5	<18	341

*Each experiment performed since the start of experimental work under Contract NAS 7-473 has been numbered in order and is frequently referred to by its number in the reports. Thus, Experiment 77 is the 77th experiment performed under this contract.

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

The vapor of the adduct was then transferred to a glass trap cooled to the NBP of liquid N_2. After the transfer was complete, the trap was allowed to warm to room temperature and the whitish-gray adduct sublimed.

The results of the vapor pressure measurement demonstrate that the $ClF_3 \cdot BF_3$ adduct is volatile enough to meet the requirements of an OF_2 gelling agent.

(2) Storage Test of OF_2 Gelled with $ClF_3 \cdot BF_3$

The purpose of the experimental work described below was to determine if the $ClF_3 \cdot BF_3$ adduct gelled OF_2 and if a satisfactory gel was obtained to measure the storage properties of the gel.

Experiment 90

The reagent holding tanks were evacuated and 129.5 gm (1.4 moles) of ClF_3 was added to the tanks as a vapor. The ClF_3 was then condensed into a stainless steel tube which was cooled with liquid N_2. The valve leading to the cold finger was closed and 96.4 gm (1.4 moles) of BF_3 vapor was added to the tanks. This material was condensed into the cold finger. The mixture of ClF_3 and BF_3 was allowed to warm to room temperature and was stored for 48 hr to ensure that the adduct had formed.

The $ClF_3 \cdot BF_3$ adduct was diluted with He, 30 volumes of HE to 1 volume of adduct. This blend was injected into liquid N_2 in the usual manner. This addition of

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

the adduct required 30 min; 187 gm of adduct was passed into the liquid N_2. The particles prepared were a pale yellow. When the sample had been sparged down to a volume of 650 cc, a thin gel was obtained. The settling rate was then measured. No settling occurred in 1/2 hr.

A second batch of $ClF_3 \cdot BF_3$ adduct was prepared as described above, except that the reagent was not stored for 48 hr. The 168 gm of adduct was injected into the mixture of liquid N_2 and adduct particles formed. A definite gel was obtained when the sample volume was 1400 cc.

Initially, 210 cc of liquid OF_2 was added to the mixture of adduct particles and liquid N_2. As the OF_2 addition proceeded, the sample turned pink and then violet in color. When 550 cc of OF_2 had been added, the sample was a deep purple color. After all of the liquid N_2 had been sparged off, the gelled OF_2, volume 550 cc, possessed considerable structure and was a deep violet color. The gel showed no evidence of settling over a two hr period.

Using a driving pressure of 1.25 psi, 400 cc of the gelled OF_2 was transferred to the storage vessel. Gel hang-up on the mixing vessel walls was negligible. The storage vessel was sealed and the storage test started. Figure 1 shows the gel in storage on Day 1. Figure 2 shows the gel after 30 days of storage.

Figure 1. Oxygen Difluoride Gel - 1st Day Storage at -196°C (139°R)
Gelant: $ClF_3 \cdot BF_3$ (ca. 12 wt%)

Figure 2. Oxygen Difluoride Gel - 30th Day Storage at -196°C (139°R)
Gelant: $ClF_3 \cdot BF_3$ (ca. 12 wt%)

III, 1 Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

During the storage test, the gel was inspected daily for signs of degradation. At no time was there any sign of exudate, sweating or gel settling. The appearance of the gel did not change in any way during the storage test.

Upon completion of the storage test, the gel was slowly warmed to -145°C, (230°R), the normal boiling point of OF_2. As the gel warmed its volume increased to 425 cc without any evidence of gel degradation. The gel at -158°C (207°R) is shown in Figure 3; note that clumps of the gel, indicative of structure, are spattered on the wall of the storage vessel between the 425 and 500 cc mark.

The gel was held at its normal boiling point for 1 hr; there was no evidence of gel degradation. The gel was grayish-purple in color at the normal boiling point of OF_2. The gelling agent remaining after the OF_2 had been boiled off was then weighed; 100 gm of gelling agent was recovered. This corresponds to the gelling agent concentration of 12 wt%. However, even though the sample weighed was at 0°C, a strong odor of OF_2 was present and the particles had a blue-gray cast. This indicates that the $OF_2 \cdot ClF_3 \cdot BF_3$ complex involved in the gelation mechanism had not completely decomposed. Therefore, the value obtained by weighing the gelant $ClF_3 \cdot BF_3$ was too high and the calculated concentration of 12 wt% attributed to the $ClF_3 \cdot BF_3$, which is based on this weight, is certainly higher than the true value. The actual concentration of $ClF_3 \cdot BF_3$ adduct would be the only portion of the system which would have a measurable effect on performance. Any OF_2 complexed with the adduct would behave as essentially pure OF_2 during the combustion process.

The results of this experiment demonstrated that one of the most important objectives of this program, the preparation of gelled OF_2 which is stable at 1-g for at least 30 days had been accomplished.

Figure 3. Oxygen Difluoride Gel at -160°C (207°R)
Gelant: $ClF_3 \cdot BF_3$ (ca. 12 wt%)

III, 1 Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

(3) Flow Tests of OF_2 Gelled with $ClF_3 \cdot BF_3$

Experiment 97

The objective of this experiment was to measure the flow properties of gelled OF_2.

A total of 266 gm of $ClF_3 \cdot BF_3$ adduct diluted with 34 volumes of He was injected into liquid N_2 in the usual manner. Based on previous measurements, 43% (114.6 gm) of the adduct was captured in the form of fine particles by liquid N_2; a thick gel was obtained at a volume of 1000 cc. Subsequently, 1100 cc of OF_2 was added to the mixture and the sample turned a deep purple color when the OF_2 was stirred into the mixture of liquid N_2 and $ClF_3 \cdot BF_3$ particles. The liquid N_2 was then sparged off with He while the sample was being vigorously stirred.

An excellent gel of OF_2 was obtained after the liquid N_2 was removed. The gel was then flowed at four different gelant concentrations and at various pressure drops between 2.0 psi and 9.0 psi. Forty-eight flow tests were conducted.

A second batch of gelled OF_2 was prepared as described above and an excellent OF_2 gel, 650 cc, was obtained. Seven flow tests were conducted at one gelant concentration. Then the transfer line clogged because of a malfunction in the liquid N_2 supply to the transfer line jacket. A discussion of the results obtained and their significance is presented below.

III, 1 Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

Two parameters are measured during a flow experiment, i.e., the ΔP across the tubing and the flow rate. These two parameters are plotted in the form of $\frac{D\Delta P}{4L}$ versus $\frac{8V}{D}$, where D is the diameter of the tubing in cm, L is the effective length of the tubing in cm, ΔP is the pressure drop in dynes/cm^2, and V is the velocity at which the gel is transferred through the tubing in cm/sec. This velocity is calculated from the measured flow rate. The term $\frac{D\Delta P}{4L}$ is commonly referred to as the shear stress, and the term $\frac{8V}{D}$ is referred to as the shear rate. The ratio of shear stress divided by the shear rate is the apparent viscosity of the fluid at that particular flow rate. The plot of $\frac{D\Delta P}{4L}$ versus $\frac{8V}{D}$ produces a curve which is referred to as the "characteristic flow curve" for the fluid being tested.

The results of the gelled OF_2 flow tests are presented in Tables II through VI. The characteristic flow curves of gelled OF_2 at various gelant concentrations are shown in Figure 4. The characteristic flow curve for water, which was measured in the same flow loop, is presented for comparison. The water was flowed in the turbulent region.

The data demonstrate that, at higher flow rates, the gels have shear-thinned to a point where their flow behavior is approaching that of water. This can be seen by comparing the characteristic flow curves of the gels and water. As the data show in most cases, the apparent viscosity is not decreasing with increasing shear rates. Therefore, it is probable that the gels were flowed in the turbulent region because the slope of their "characteristic flow curves" is similar to the slope of the flow curve of water. Additional discussion of the flow behavior of particulate gels is presented in Section III,4,(a).

If it had been possible to flow the gels at very low shear rates, less than 20 sec^{-1}, the extreme shear-thinning that is typical of

TABLE II

FLOW CHARACTERISTICS OF GELLED LIQUID OF_2 - GELLING AGENT $ClF_3 \cdot BF_3$

Concentration of Gelling Agent - 5.9 wt%

Run No.	Δ Pressure psi	Δ Pressure dynes/cm^2	Flow Parameters: Rate cc/sec	Flow Parameters: Velocity cm/sec	Shear Rate, $\frac{8V}{D}$ sec^{-1}	Shear Stress, $\frac{D\Delta P}{4L}$ dynes/cm^2	Apparent Viscosity $\frac{D\Delta P}{4L} / \frac{8V}{D}$ poise
15, 16	9.0	62.0×10^4	128	268	2750	460	0.17
14, 13	7.8	5.38×10^4	118	247	2530	399	0.16
12, 11	5.5	37.9×10^4	99	208	2130	281	0.13
6	5.2	35.8×10^4	95	198	2030	266	0.13
1, 2	4.6	31.7×10^4	87	182	1870	235	0.13
10, 9	3.6	24.8×10^4	78	164	1680	186	0.11
7, 8	2.8	19.3×10^4	63	132	1360	140	0.10
11	1.6	11.0×10^4	41	87	890	82	0.09

TABLE III

FLOW CHARACTERISTICS OF GELLED LIQUID OF_2 - GELLING AGENT $ClF_3 \cdot BF_3$

Concentration of Gelling Agent - 8.3 wt%

Run No.	Δ Pressure psi	Δ Pressure dynes/cm^2	Flow Parameters: Rate cc/sec	Flow Parameters: Velocity cm/sec	Shear Rate, $\frac{8V}{D}$ sec^{-1}	Shear Stress, $\frac{D\Delta P}{4L}$ dynes/cm^2	Apparent Viscosity $\frac{D\Delta P}{4L} / \frac{8V}{D}$ poise
1	5.0	34.5×10^4	83	174	1800	256	0.14
2	3.5	24.1×10^4	66	139	1430	179	0.13
3,4	2.3	15.9×10^4	46	101	992	118	0.12
5,6	2.0	13.8×10^4	42	87	910	104	0.12

TABLE IV

FLOW CHARACTERISTICS OF GELLED LIQUID OF_2 - GELLING AGENT $ClF_3 \cdot BF_3$

Concentration of Gelling Agent - 9.0 wt%

Run No.	Δ Pressure psi	Δ Pressure dynes/cm^2	Flow Parameters Rate cc/sec	Flow Parameters Velocity cm/sec	Shear Rate, $\frac{8V}{D}$ sec^{-1}	Shear Stress, $\frac{D\Delta P}{4L}$ dynes/cm^2	Apparent Viscosity $\frac{D\Delta P}{4L} / \frac{8V}{D}$ poise
31, 32	10.0	68.9×10^4	129	270	2770	512	0.18
24, 25	7.5	51.7×10^4	102	214	2190	384	0.17
22, 23 30	6.0	41.4×10^4	88	184	1890	307	0.16
20, 21	4.0	27.6×10^4	62	131	1340	207	0.15
29, 28	3.3	22.8×10^4	64	134	1380	170	0.12
26, 27	2.2	15.2×10^4	43	90	920	112	0.12

TABLE V

FLOW CHARACTERISTICS OF GELLED LIQUID OF_2 - GELLING AGENT $ClF_3 \cdot BF_3$

Concentration of Gelling Agent - 12.5 wt%

Run No.	Δ Pressure psi	Δ Pressure dynes/cm^2	Flow Parameters Rate cc/sec	Flow Parameters Velocity cm/sec	Shear Rate, $\frac{8V}{D}$ sec^{-1}	Shear Stress, $\frac{D\Delta P}{4L}$ dynes/cm^2	Apparent Viscosity $\frac{D\Delta P}{4L} / \frac{8V}{D}$ poise
37, 38	8.0	55.2×10^4	97	203	2080	409	0.20
35, 36	7.0	48.3×10^4	82	171	1750	358	0.20
34	5.0	34.5×10^4	53	112	1150	256	0.22
35	4.5	31.0×10^4	45	93	960	230	0.24
41, 42	3.3	22.8×10^4	43	91	930	170	0.18
39, 38	2.8	19.3×10^4	27	56	580	143	0.25

TABLE VI

FLOW CHARACTERISTICS OF GELLED LIQUID OF_2 - GELLING AGENT $ClF_3 \cdot BF_3$
Concentration of Gelling Agent - 15.6 wt%

Run No.	Δ Pressure psi	Δ Pressure dynes/cm^2	Flow Parameters: Rate cc/sec	Flow Parameters: Velocity cm/sec	Shear Rate, $\frac{8V}{D}$ sec^{-1}	Shear Stress, $\frac{D\Delta P}{4L}$ dynes/cm^2	Apparent Viscosity $\frac{D\Delta P}{4L} / \frac{8V}{D}$ poise
48, 49	8.0	55.2×10^4	74	154	1590	409	0.26
46, 47	6.0	41.4×10^4	62	130	1330	307	0.23
43, 44, 45	4.0	27.6×10^4	33	68	702	205	0.29
50, 51	3.0	20.7×10^4	33	69	708	153	0.22
52	2.2	15.2×10^4	21	44	451	112	0.25

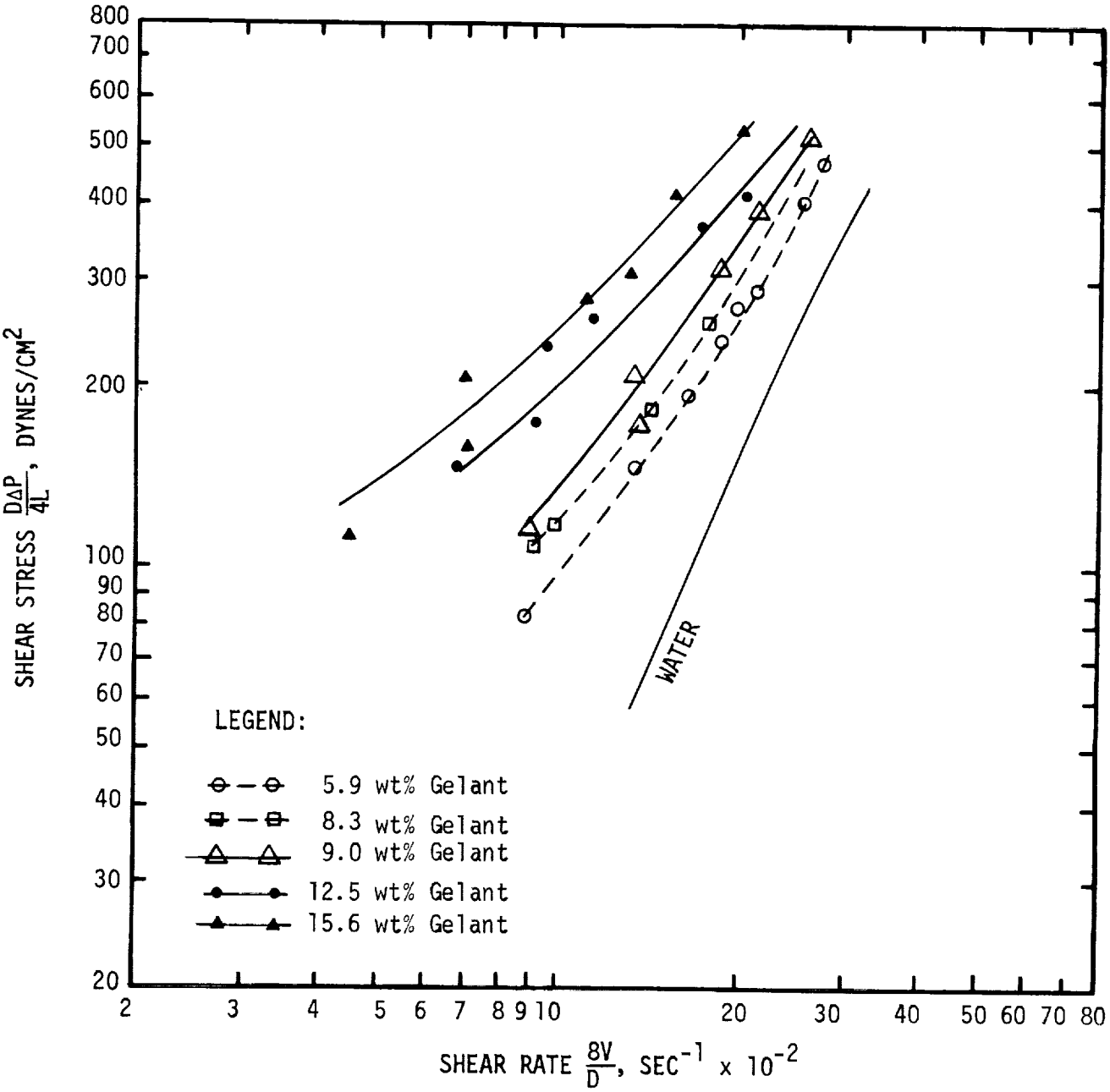

Figure 4. Characteristic Flow Curves of OF_2 Gelled with $ClF_3 \cdot BF_3$ At Various Gelant Concentrations

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particulate gels at low shear rates with only small increases in shear rate would have been seen. Flow data in this shear rate region are presented in Reference 2, Page 95.

(4) Evaluation of Other Gelants for OF_2

As previously discussed, results of the measurement of the storage properties of OF_2 gelled with ClF_3 particles, completed during the last supplement to this contract, demonstrated that this gelled oxidizer formulation did not posses sufficient storage stability to meet the anticipated use requirements. Therefore, work was initiated to evaluate other gelling agents for liquid OF_2.

The first group of reagents evaluated were other interhalogens such as bromine pentafluoride (BrF_5), etc. While these materials would be analogous to ClF_3 as gelants, their substantially higher melting points and higher molecular weight should tend to decrease the solubility of the gelant in liquid OF_2. Reduced solubility would enhance the possibility of preparing a gel that would meet the storage requirements. The results of the evaluation of BrF_5 as a gelling agent for OF_2 are reported below.

Experiment 76

A total of 574 gm of BrF_5 vapor, diluted with He, was injected into liquid N_2 in the usual manner. A thin gel of liquid N_2 was obtained at a volume of 535 cc. Then 450 cc of OF_2 was added to the mixture and the liquid N_2 was sparged off with He.

The OF_2 gel was very thin and slight settling was observed in 5 min. Because the gel was not satisfactory, no attempt was made to store the gel. The gel contained 38 wt% BrF_5.

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It was concluded that BrF_5 is not a satisfactory gelling agent for OF_2 because a prohibitive quantity of gelling agent is required for OF_2 gelation.

The second interhalogen evaluated as a gelling agent for use with OF_2 was bromine trifluoride (BrF_3).

Bromine trifluoride melts at 8.8°C and has a vapor pressure of 5.5 mm Hg at 20°C. Therefore, the normal technique of adding the reagent to an evacuated holding tank, diluting it with He, and injecting the mixture into liquid N_2 was no longer practical. Over the course of several experiments, a technique was developed for injecting low vapor pressure, relatively high melting point materials below the surface of liquid N_2.

The BrF_3 addition equipment consisted of a tank holding liquid BrF_3 which was fitted with the appropriate tubes and valves so that a stream of He could be bubbled through the liquid BrF_3. In addition, a preheater to warm the incoming He, a tank heater to heat the liquid BrF_3, and a line heater to maintain the He-BrF_3 vapor mixture at the desired temperature were installed. As the hot BrF_3 corroded the stainless-steel injection tube, a new injection tube was fabricated using nickel tubing for BrF_3 service. The experimental work is discussed below.

Experiment 88

The BrF_3 tank was heated to 67°C, the preheater to 86°C, and the line leading to the mixing vessel to 149°C. At 67°C the vapor pressure of BrF_3 is 1.5 psia. After the temperatures were stabilized, He flow through the BrF_3 tank was started and continued for 220 min. The pressure in the BrF_3 tank

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was 50 psig, and the pressure drop across the injection tube orifice was 49 psi. A total of 509 gm of BrF_3 was injected into the liquid N_2. The liquid N_2 volume was then slowly reduced by sparging the mixture with He. When the volume of the mixture of BrF_3 particles and liquid N_2 reached 660 cc, a thin gel formed.

A total of 330 cc of liquid OF_2 was added to the mixture in small increments. The mixture was vigorously stirred between each addition. The sample was then sparged with He until the liquid N_2 was removed and a thin gel was obtained. As the gel showed evidence of settling after 1/2 hr storage, no attempt was made to run a 30-day storage test. After the OF_2 was evaporated, 327 gm of BrF_3 was found in the mix vessel, which corresponds to 35.8 wt% of BrF_3 in the oxidizer.

The results discussed above demonstrate that a prohibitive quantity of BrF_3 particles is required for gelation of OF_2, and that BrF_3 should be eliminated as a potential gelant candidate.

The results with the interhalogens other than ClF_3 indicated that these materials did not hold promise as candidate gelling agents for OF_2. Consequently, experimental work was directed toward the evaluation of adducts as gelling agents. Two approaches to the preparation of adduct gelants are available.

The first is the in-situ synthesis of the adduct; the second is the preparation of the adduct external to the system with subsequent addition. The first reagent selected for evaluation was BF_3 because OF_2 is a

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weak Lewis base. As BF_3 is one of the strongest Lewis acids available, the feasibility of preparing a Lewis salt in-situ can be rapidly determined by attempting to prepare the $BF_3 \cdot OF_2$ adduct in liquid N_2. The results of the experimental work done to determine the feasibility of this approach is presented below.

Experiment 74

The first step in this experiment was to evaluate the behavior of BF_3 in liquid N_2. Thirty gm of BF_3 vapor, diluted with He, was injected in the usual manner into liquid N_2. No gel was obtained at any concentration. The measured melting point range of the BF_3 in the apparatus was -132 to -124°C. The literature value is -127°C. After the melting point measurement was completed, the apparatus was warmed and the BF_3 sparged out of the equipment.

One-thousand cc of liquid N_2 was added to the gelling vessel and 48 cc of OF_2 was dissolved in liquid N_2. Additional liquid N_2 was added to bring the volume of liquid to approximately 1800 cc. Sixty-one gm of BF_3 vapor, diluted with He, was injected in the usual manner into the liquid N_2-OF_2 solution.

The solution was then slowly allowed to evaporate. No evidence of gel formation was observed at any volume. The measured melting point range of the solid in the apparatus was -128 to -101°C.

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The relatively wide measured melting point range compared to pure BF_3 and the increase in the melting point indicated that a portion of the OF_2 may have reacted with the BF_3 to form the desired adduct. It was possible that the reaction had not gone to ccmpletion because of the low temperature of the system. Consequently, additional experimental work was required to determine if BF_3 formed an adduct with OF_2.

Experiment 75

When two gases are mixed, the pressure of the system will be equal to the sum of the individual pressures if no interaction or reaction occurs. However, if there is a reaction, i.e., adduct formation, the pressure of the system will be substantially lower than the sum of the two individual pressures. Therefore, the measurement of a negative deviation in pressure from ideality at various temperatures of a mixture of OF_2 and BF_3 will provide conclusive evidence of adduct formation.

Equal molar quantities of OF_2 and BF_3 were mixed together and the pressure measured at various temperatures. The results are presented in Table VII.

TABLE VII

PRESSURE OF AN EQUAL MOLAR MIXTURE OF OF_2 AND BF_3

Temperature °C	Measured Pressure mm Hg	Calculated Pressure Assuming no Adduct Formation mm Hg
24.0	2761	2738
0.0	2590	2561
-78.5	1928	1893
-196.0	12	--

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The results presented in Table VII show that no negative deviation in pressure occurred. Therefore, it is concluded that BF_3 and OF_2 do not form a stable adduct at temperatures of -78°C and above.

The $ClF_3 \cdot BF_3$ adduct had been prepared during the course of work done at Aerojet on the development of new oxidizers. It was believed that there was a possibility that ClF_3 particle growth could be inhibited if the ClF_3 molecules are "tied-up" by a second species, i.e., BF_3, as they dissolve from the smaller particles and migrate to the larger particles. The experimental work done to determine if this approach would stabilize the gelled OF_2 is presented below.

Experiment 86

A total of 183 gm of ClF_3 vapor diluted with He, 50 volumes of He to 1 volume of ClF_3 vapor, was injected into liquid N_2 in the usual manner. A thick gel was obtained at a volume of 1500 cc. Then 36.7 gm of BF_3 vapor diluted with He, 50 volumes of He to 1 volume BF_3 vapor, was injected into the mixture of liquid nitrogen and ClF_3 particles. The system was then sparged down with He until the volume reached 1375 cc and then stored under a 2-psig head of He overnight (16 hr).

It was not possible to measure a settling rate directly because 155 cc of the sample was lost by evaporation. However, settling could not exceed the quantity lost by evaporation as no exudate was observed after the 16 hr storage. There was no evidence of gel degradation or

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reaction between the ClF_3 and BF_3 particles while the particles were in liquid N_2.

Next, 650 cc of OF_2 was added to the mixture in small increments and the sample was vigorously stirred after each addition. After the initial OF_2 addition the sample began to develop a strong pink color which became progressively darker as the OF_2 addition continued.

Upon completion of the OF_2 addition, the sample was gently sparged down with He. At a volume of 900 cc (250 cc liquid N_2 and 650 cc liquid OF_2) the gel appeared to be much thinner than before. White specks of material the size of a pin head could be seen distributed throughout the gel. Gentle sparging was continued until the gel volume reached 600 cc. The settling rate was measured; the gel settled 10 cc in 1 hr.

As it was apparent that the presence of BF_3 in the OF_2 gelled with ClF_3 particles accelerated gel degradation, the sample was discarded. It was not possible to measure precisely the quantity of gelant present in the system during the disposal procedure because a portion of the ClF_3 had reacted with the BF_3 to form the adduct which is a solid. However, based on previous experiments, the sample composition at a volume of 600 cc was 10 wt% ClF_3, 2 wt% BF_3, and 88 wt% OF_2.

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It is believed that only a small portion of the BF_3 reacted to form the $ClF_3 \cdot BF_3$ adduct. As the adduct was prepared with ease in later experiments conducted under quite different conditions, it appears that this reaction does not proceed to completion if one of the reactants is in the solid state. It is concluded from the results of this experiment that the presence of BF_3 in OF_2 gelled with ClF_3 accelerates the rate of ClF_3 particle growth and this causes rapid gel degradation. The development of the strong pink color in the sample during the OF_2 addition demonstrates that a chemical reaction was taking place.

The next candidate gelling agent evaluated was the $ClF_3 \cdot BF_3$ adduct. The experimental work which led to the preparation of gelled OF_2 which met the objectives of this program and the subsequent characterization of the gel was discussed previously in this report in Section III,1,a.

b. Phase 2, Gelation of B_2H_6 with Selected Gelants and Determination of Gelled B_2H_6 Storage and Flow Properties

Two gelling agents were extensively studied for use with B_2H_6 during this program. The first was trimethylaminoborane, $(CH_3)_3N \cdot BH_3$, and the second was trimethylamino·boron trifluoride, $(CH_3)_3N \cdot BF_3$. The experimental work with trimethylamino·boron trifluoride will be reported first because this work resulted in the preparation of gelled B_2H_6 which met the program objectives.

(1) Properties of $(CH_3)_3N \cdot BF_3$

To ensure that the gelling agent selected will not impair restart capability, it is necessary that the gelling agent be volatile under the conditions that would exist in a rocket engine immediately after shutdown. Consequently, if information regarding the volatility of a candidate gelling

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agent was not readily available in the literature, the vapor pressure of the candidate gelant was measured before it was evaluated as a gelant. The results of the measurement of the volatility of $(CH_3)_3N \cdot BF_3$ are presented below.

> Equal molar quantities of trimethylamine and boron trifluoride were mixed in a steel vessel and the vapor pressure of the adduct formed was measured. The vapor pressure is less than 1 mm Hg at room temperature.

However, the adduct may begin to dissociate at elevated temperatures and produce a steep vapor pressure curve, i.e., a rapidly increasing vapor pressure with increasing temperature. If so, the material may be volatile enough to meet the requirements of this program under the conditions that would exist in a rocket engine injector immediately after shutdown. Consequently, the NASA Technical Manager was contacted and requested to supply information regarding the anticipated temperature environment under these conditions.

The Technical Manager replied that, during the shutdown transient, heat soak-back would raise the injector's temperature to a maximum of 550°F and then the injector temperature would rapidly fall off. A plot of the data supplied showed that the mean injector temperature would be 336°F during the first 4 min after shutdown.

> The sample of trimethylamino·boron trifluoride was heated to 336°F and then quickly exposed to a vacuum. Under vacuum conditions, the trimethylamino·boron trifluoride (22 gm) was quantitatively transferred from the heated portion

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of the apparatus to a Dry Ice trap in less than 4 min.

The results of this experiment demonstrated that trimethylamino·boron trifluoride possesses sufficient volatility to meet the requirements of this program.

(2) Storage Test of B_2H_6 Gelled with $(CH_3)_3N \cdot BF_3$

The purpose of the experimental work described below was to measure the storage properties of liquid B_2H_6 gelled with $(CH_3)_3N \cdot BF_3$.

Experiment 92

The mixing vessel was cooled to -182°C and 2000 cc of methane was condensed in the vessel; 18.6 gm of trimethylamine was added to the methane by injecting it through the injection tube. Then 21.4 gm of BF_3 was injected into the mixture. The sample was held overnight and some settling was noted. Therefore, an additional 24 gm of BF_3 was added to the mixture. The sample was then sparged down to a volume of 850 cc and held for 20 hr. During the first 4.5 hr, the gel settled 50 cc; no further settling occurred. Then 700 cc of B_2H_6 was added to the surface of the mixture of methane and trimethylamino·boron trifluoride particles and then the mixture was vigorously stirred.

As the mixing started, the gel changed color from white to beige and became translucent. The liquid methane was then sparged off with a stream of helium.

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When the mixture volume reached 700 cc, essentially all B_2H_6, an excellent gel was obtained. When sparging stopped, helium bubbles were seen to be suspended throughout the gel.

The gel was warmed to -156°C (210°R) and vigorously sparged with He until the volume was reduced to 500 cc. This was done to ensure that all of the methane was removed from the sample and then 340 cc of the gel was transferred to the storage vessel. During the transfer some coring was experienced; it was not serious, however.

The gelling agent concentration was 6.7 wt%.

During the first 33 days of storage, the gel was stored at -156°C (210°R); the gel showed no evidence of deterioration. Figure 5 shows the gel on the first day of storage; Figure 6 shows the gel on the thirty-third day of storage. Over the course of this portion of the storage test, approximately 20 cc of gel (5.9%) was lost by evaporation.

After the completion of this portion of the test, the temperature was raised at a rate of between 1.7°C (3°R) and 3°C (5°R) per day. Until the gel reached -132°C (255°R) which took 13 days, there was no evidence of gel degradation. During the course of the 13 days, an additional 25 cc was lost by evaporation.

When the gel temperature was raised to -127°C (263°R), a liquid layer of 10 to 15 cc formed on the surface of the gel. The gel below the liquid layer still possessed considerable structure because the He bubbles

Figure 5. Gelled B_2H_6 - Storage Test 1st Day, Temperature -156°C (210°R)
Gelant: Trimethylamino-boron Trifluoride

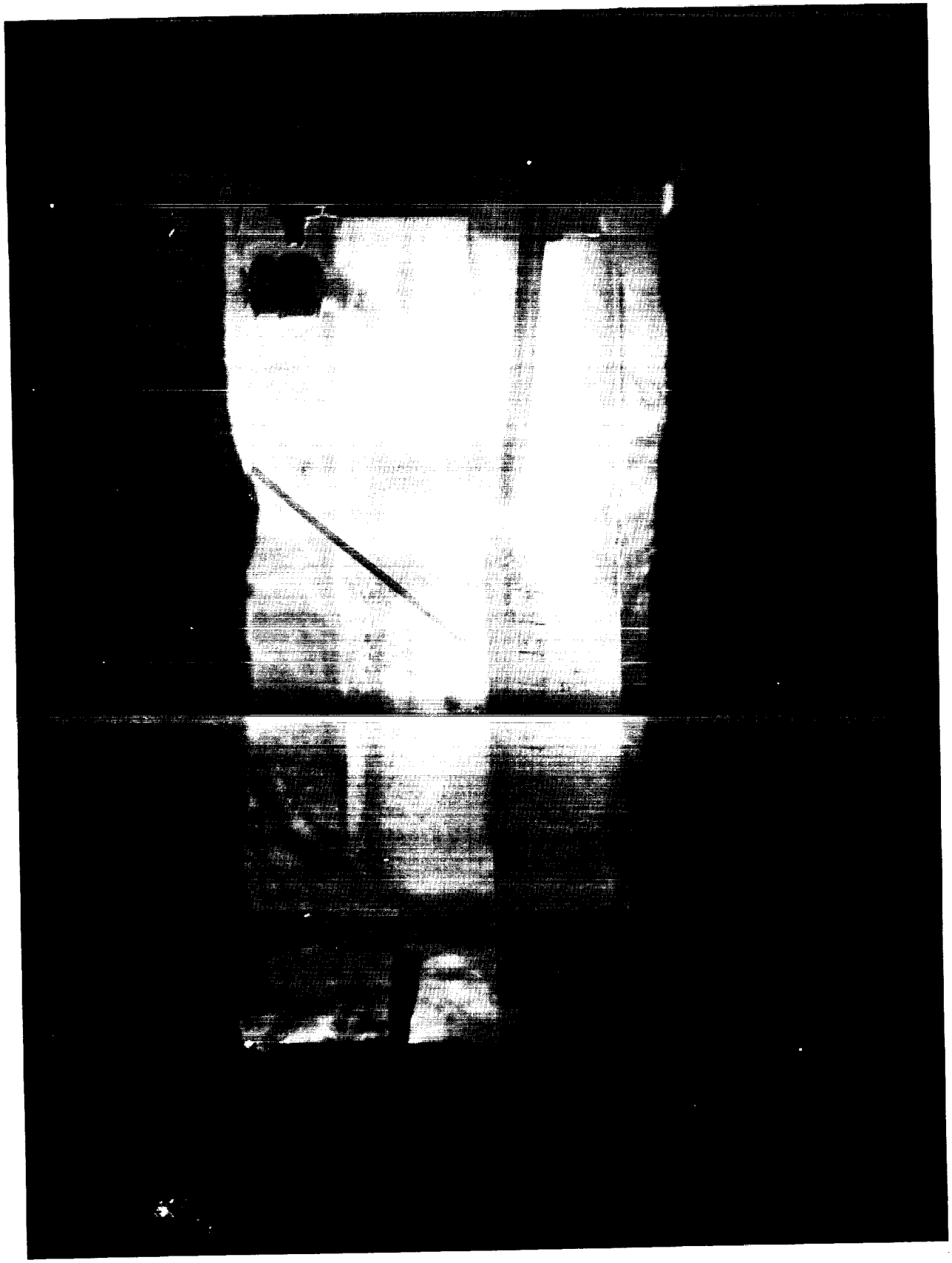

Figure 6. Gelled B_2H_6 - Storage Test 33rd Day, Temperature -156°C (210°R)
Gelant: Trimethylamino·boron Trifluoride

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dispersed throughout the gel showed no evidence of rising in the gel. Over the next 4 days, the temperature was raised to -112°C (290°R). The liquid layer above the gel increased in volume to about 30 cc. The gel volume remained constant and no motion of the He bubbles, which would indicate gel degradation, was observed; in fact, the He bubbles remained in the gel until the temperature reached -92°C (326°R), the normal boiling point of diborane.

The experimental results described above demonstrate that gelled B_2H_6 gelled with trimethylamino·boron trifluoride is stable, with respect to exudate formation, to temperatures as high as -132°C (255°R) for 46 days. In addition, as the gel below the exudate layer observed at temperatures above -127°C (263°R) was stable, it is possible that the gel is stable at temperatures as high as -92°C (326°R). Therefore, one of the objectives of this program, which was the preparation of gelled B_2H_6 which is stable at 1 g for 30 days or longer, had been accomplished.

A possible cause of the exudate formation at elevated temperatures is failure of the gel particles to move as rapidly as the liquid during thermal expansion. This can occur because B_2H_6 undergoes a 30% increase in volume when the temperature increases from -156 to -112°C (210 to 290°R). If the gel were prepared at its use temperature, it might well be possible that the gel would remain stable with respect to exudate formation.

Earlier in the program a gel of diborane gelled with 4.7 wt% $(CH_3)_3N·BF_3$ was prepared and the storage properties measured. The experimental procedure and results are discussed below.

Experiment 89

The mixing vessel was cooled to -110°C and 16.1 gm of liquid trimethylamine was added. The system was

then pressurized to 5 psig with methane and then cooled to -182°C, and the liquefaction of the CH_4 started. The mixture of liquid methane and trimethylamine was frequently stirred as 2000 cc of methane was added to the gelling vessel. Only a portion of the trimethylamine dissolved in the methane, and solid trimethylamine was present when the boron trifluoride addition began.

Boron trifluoride vapor, 37.4 gm, diluted with 25 volumes of He was injected into the mixture of methane and trimethylamine. After the BF_3 addition had been completed the volume of the mixture was reduced from 2000 cc to 1200 cc, at which point the mixture started to show signs of thickening, and at a volume of 1050 cc the sample was a definite gel. The gelled methane was held over the weekend and no evidence of settling was observed. However, as 100 cc of material was lost by evaporation the result is not completely conclusive.

The sample of gelled methane was sparged until the volume reached 630 cc and then 630 cc of B_2H_6 was added in small increments. The sample was vigorously stirred during the B_2H_6 addition. The mixture of methane, diborane, and trimethylamino·boron trifluoride was then sparged with He until the apparent volume was reduced to 660 cc. At this point most of the methane had been removed, and the diborane gel was translucent in appearance as compared to the opaque appearance of the earlier diborane gels prepared with trimethylaminoborane.

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As the gel prepared had considerable structure, it was decided to demonstrate the storability characteristics of the gel. Approximately 550 cc was transferred through a 3/8-in. line to the storage vessel without difficulty and the pressure drop required was less than 5 psi.

The gelled B_2H_6 was a beige translucent material. The gel initially had a high degree of structure and various size He bubbles were dispersed throughout the gel. Gelant concentration, measured at the conclusion of the storage test was 4.7 wt%. Table VIII presents the results of the storage test and Figure 7 shows the gel on the first day of storage.

TABLE VIII

STORAGE TEST - GELLED B_2H_6

Gelant: Trimethylamino·boron Trifluoride
Gelant Concentration: 4.7 wt%
Test Temperature: -156°C (210°R)

Time Days	Total Volume cc	Gel Volume cc	Exudate cc	Remarks
0	560(1)	560	0	(1) The most likely cause of the decreasing total volume was the loss of the He bubbles that were dispersed throughout the gel.
1	540	510	30	
2	535	490	45	
3	535	480	55	
10	520	469	55	
15	480(2)	440	40	(2) System developed a small leak and B_2H_6 was being lost by evaporation.
20	450	430	20	
25	440	410	30	
28	437	395	42	

Test Terminated

Figure 7. Diborane Gel, 1st Day Storage at -156°C (210°R)
Gelant: Trimethylamino·boron Trifluoride

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In Figure 8, the gel is shown at the conclusion of the storage test. After warming to -93°C (325°R), the gel still possessed some structure. At the normal boiling point of diborane, the gel had completely broken and the gelling agent had settled.

The results of the storage test indicate that the gel does not degrade drastically at -156°C (210°R). As the gelant concentration was quite low, 4.7 wt%, the storage test was repeated at a higher gelant concentration to determine if a more heavily loaded B_2H_6 gel would be stable.

(3) Flow Tests of B_2H_6 Gelled with $(CH_3)_3N{\cdot}BF_3$

Two batches of gelled B_2H_6 gelled with $(CH_3)_3N{\cdot}BF_3$ were prepared as previously described and the flow properties measured at various gelant concentrations and temperatures. The results of the gelled B_2H_6 flow tests are presented in Tables IX through XIII. The characteristic flow curve of gelled B_2H_6 at various temperatures and concentrations is shown in Figure 9. The characteristic flow curve for water, which was measured in the same flow loop, is presented for comparison. The water was flowed in the turbulent region. The parameters measured and the manner in which the results are presented is discussed in Section III,1,a,(3).

The data show that the gel exhibits the extreme shear-thinning typical of particulate gels and that the resistance to flow is less than that of water at the higher shear rates. In addition, the data show that the gel gradually loses its ability to regain its structure after repeated shearing. This loss of structure because of repeated shearing is gradual and is not a serious defect because in use the gel would only be sheared twice, once when the propellant tank is loaded, and then when the propellant is used. The horizontal orientation of the characteristic flow curve at low shear rates

Figure 8. Diborane Gel, 28th Day Storage at -156°C (210°R)
Gelant: Trimethylamino·boron Trifluoride

TABLE IX

FLOW CHARACTERISTICS OF GELLED LIQUID B_2H_6 - GELLING AGENT $(CH_3)_3N \cdot BF_3$

Temperature -156°C (217°R)
Concentration of Gelling Agent - 9.5 wt%

Run No.	Δ Pressure psi	Δ Pressure dynes/cm^2	Flow Parameters Rate cc/sec	Flow Parameters Velocity cm/sec	Shear Rate, $\frac{8V}{D}$ sec^{-1}	Shear Stress, $\frac{D\Delta P}{4L}$ dynes/cm^2	Apparent Viscosity, $\frac{D\Delta P}{4L} / \frac{8V}{D}$ poise
8,11, 12	2.3	15.9×10^4	109	229	2350	99	0.042
9,10	2.2	15.2×10^4	99	207	2120	94	0.045
1,2, 3	1.8	12.4×10^4	87	182	1870	77	0.041
6,7	1.4	9.6×10^4	75	158	1610	60	0.037
4,5	1.0	6.9×10^4	43	89	915	43	0.047
13,14	0.8	5.5×10^4	30	63	650	34	0.053

TABLE X

FLOW CHARACTERISTICS OF GELLED LIQUID B_2H_6 - GELLING AGENT $(CH_3)_3N \cdot BF_3$

Temperature -144°C (232°R)
Concentration of Gelling Agent - 10.6 wt%

Run No.	Δ Pressure psi	Δ Pressure dynes/cm^2	Flow Parameters Rate cc/sec	Flow Parameters Velocity cm/sec	Shear Rate, $\frac{8V}{D}$ sec^{-1}	Shear Stress, $\frac{D\Delta P}{4L}$ dynes/cm^2	Apparent Viscosity, $\frac{D\Delta P}{4L} / \frac{8V}{D}$ poise
25,26	1.9	13.1×10^4	104	219	2250	82	0.036
23,24	1.8	12.4×10^4	88	185	1900	77	0.040
20,21 22	1.4	9.6×10^4	75	156	1600	60	0.037
19	1.0	6.9×10^4	57	110	1130	43	0.038
18	0.9	6.2×10^4	54	113	1100	39	0.33
15,16 17	0.7	4.8×10^4	21	43	410	30	0.069

TABLE XI

FLOW CHARACTERISTICS OF GELLED LIQUID B_2H_6 - GELLING AGENT $(CH_3)_3N \cdot BF_3$

Temperature -127°C (262°R)
Concentration of Gelling Agent - 11.4 wt%

Run No.	Δ Pressure psi	Δ Pressure dynes/cm^2	Flow Parameters Rate cc/sec	Flow Parameters Velocity cm/sec	Shear Rate, $\frac{8V}{D}$ sec^{-1}	Shear Stress, $\frac{D\Delta P}{4L}$ dynes/cm^2	Apparent Viscosity, $\frac{D\Delta P}{4L} / \frac{8V}{D}$ poise
35,36	1.5	10.3×10^4	97	203	2080	64	0.031
33,34	1.2	8.3×10^4	65	137	1410	51	0.036
30,32	0.9	6.2×10^4	45	94	960	39	0.040
31	0.8	5.5×10^4	45	94	960	34	0.036
27,28 29	0.7	4.8×10^4	21	44	450	30	0.066
40,41	0.5	3.4×10^4	25	54	560	21	0.039
37,38 39	0.4	2.8×10^4	9.7	20	208	18	0.089

TABLE XII

FLOW CHARACTERISTICS OF GELLED LIQUID B_2H_6 - GELLING AGENT $(CH_3)_3N \cdot BF_3$

Temperature -127°C (262°R)
Concentration of Gelling Agent - 14.6 wt%

Run No.	Δ Pressure psi	Δ Pressure dynes/cm^2	Flow Parameters Rate cc/sec	Flow Parameters Velocity cm/sec	Shear Rate, $\frac{8V}{D}$ sec^{-1}	Shear Stress, $\frac{D\Delta P}{4L}$ dynes/cm^2	Apparent Viscosity, $\frac{D\Delta P}{4L} / \frac{8V}{D}$ poise
51,52	1.3	9.0×10^4	74	155	1590	56	0.035
42,43	1.2	8.3×10^4	65	137	1410	51	0.037
49,50	1.0	6.9×10^4	57	120	1230	43	0.035
46,48	0.7	4.8×10^4	37	78	803	30	0.037
44,45	0.5	3.4×10^4	23	47	480	21	0.044

TABLE XIII

FLOW CHARACTERISTICS OF GELLED LIQUID B_2H_6 - GELLING AGENT $(CH_3)_3N \cdot BF_3$

Temperature -155°C (212°R)
Concentration of Gelling Agent - 12 wt%

Run No.	Δ Pressure psi	Δ Pressure dynes/cm^2	Flow Parameters Rate cc/sec	Flow Parameters Velocity cm/sec	Shear Rate, $\frac{8V}{D}$ sec^{-1}	Shear Stress, $\frac{D\Delta P}{4L}$ dynes/cm^2	Apparent Viscosity, $\frac{D\Delta P}{4L} / \frac{8V}{D}$ poise
16	3.1	21.4×10^4	74	155	1590	133	0.084
15	3.0	20.7×10^4	79	165	1700	127	0.076
1	2.5	17.2×10^4	52	108	1110	107	0.096
3,4, 5,6, 8	2.4	16.6×10^4	54	113	1160	103	0.096
2,7	2.3	15.9×10^4	50	106	1066	99	0.091
14	2.2	15.2×10^4	11	24	243	94	0.388
12,13	2.1	14.5×10^4	13	28	282	90	0.321

Note: Flow could not be initiated at any pressure below 1.5 psi.

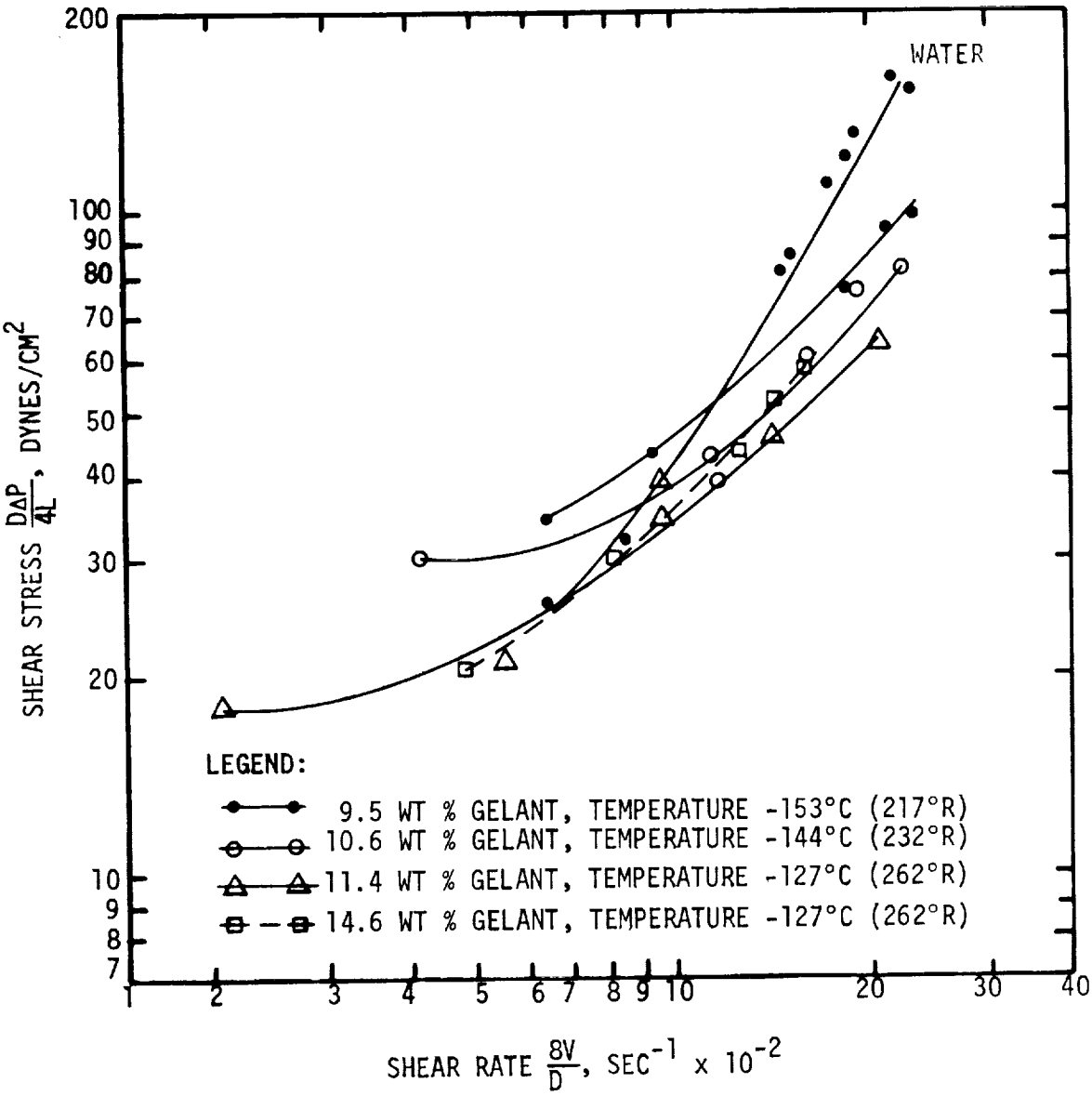

Figure 9. Characteristic Flow Curves of B_2H_6 Gelled with $(CH_3)_3N{\cdot}BF_3$ At Various Temperatures and Gelant Concentrations

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

indicates that the gel shear-thins rapidly, i.e., the viscosity of the gel decreases rapidly with increasing shear rates. At higher shear rates, the gel behavior approaches that of a Newtonian liquid flowing in the turbulent region.

The effect of gelant concentration on flow behavior is more appropriately shown in Figure 10. The characteristic flow curves were obtained with fresh gels, i.e., the gels had not been extensively sheared. Additional discussion of the flow behavior of particulate gels is presented in Section III,4,(a).

(4) Evaluation of $(CH_3)_3N{\cdot}BH_3$ as a Gelant for B_2H_6

During the previous supplement to this contract, trimethylaminoborane, an adduct, was synthesized in liquid methane by reacting trimethylamine with diborane dissolved in liquid methane. The resulting particles of trimethylaminoborane gelled liquid B_2H_6. Consequently, work was initiated at the beginning of this portion of the work to determine the storage stability of the gel at -134°C (250°R).

Experiment 79 - Experimental Procedure

The purpose of Experiment 79 was to prepare a gel of B_2H_6 with trimethylaminoborane as the gelant, and to measure the storage properties of the gel.

Initially, 1200 cc of liquid methane was added to the gelling vessel and 36 gm of B_2H_6 was dissolved in the methane. The solution was vigorously stirred and the volume brought up to 2100 cc by adding additional methane. The injection of the mixture of 50 volumes helium and 1 volume of

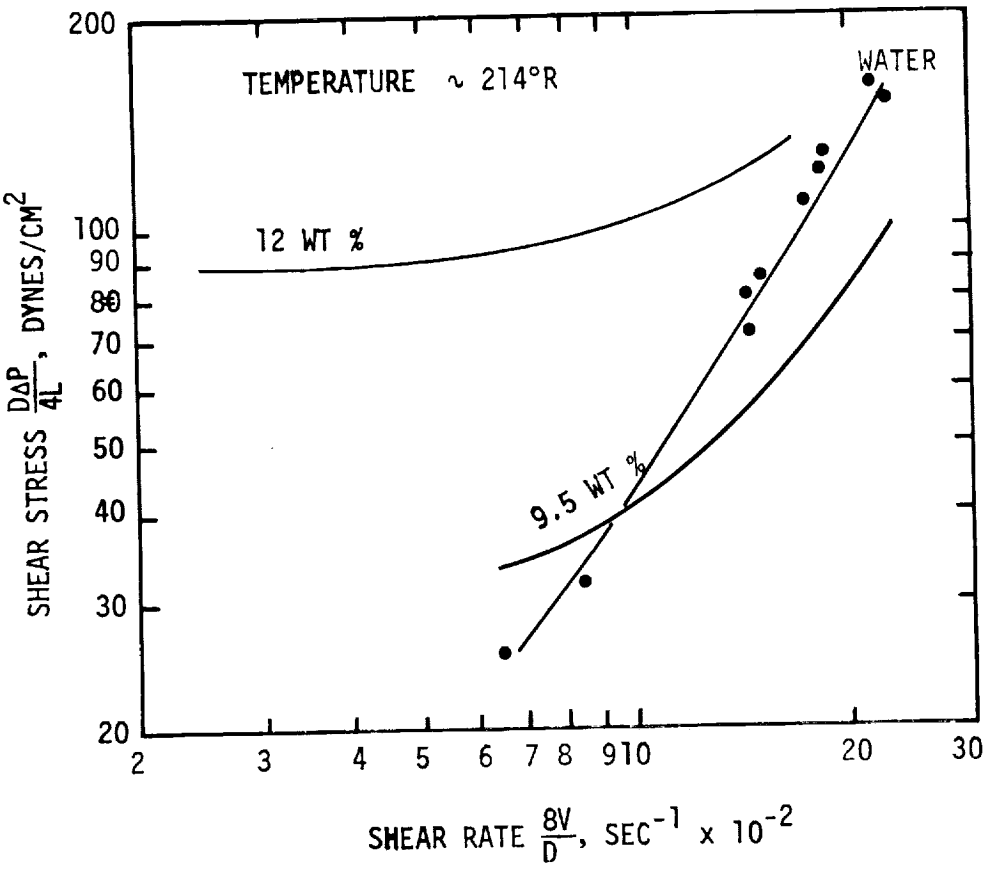

Figure 10. Characteristic Flow Curves of B_2H_6 Gelled with $(CH_3)_3N{\cdot}BF_3$

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

trimethylamine was initiated and considerable difficulty was encountered in making up the liquid methane lost be evaporation during the injection. Consequently, injection of the trimethylamine continued until the methane level reached 1000 cc and then was discontinued. The liquid methane level was then brought up to 2100 cc and the injection of trimethylamine resumed. This process was continued until 115 gm of trimethylamine had been added to the mixture of methane and diborane. The liquid methane level was then made up to 1200 cc and the sample held overnight.

The sample was then sparged with He until the level reached 1000 cc and the settling rate was measured. Very slight settling, less than 5 cc, was observed in one hour. However, as the quantity of gelled diborane required for storage was 670 cc and as these gels thicken rapidly with increasing gelant concentration, it was decided to add diborane to the mixture and sparge off the methane.

In a series of four additions, 752 cc of diborane was added to the mixture of methane and particles. Before each addition, the sample was vigorously stirred and sparged with He until the level reached 1000 cc. After the final addition, the level was reduced by sparging to 780 cc. The gelled diborane was then stored overnight (15 hr) at -156°C (210°R).

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

After 15 hr of storage in the gelling vessel at -156°C (210°R) the total volume of the sample had been reduced 30 cc by evaporation and an exudate of approximately 10 cc was observed. Therefore, it was assumed that the maximum settling that could have occurred was 40 cc. This indicated that some slight thickening of the gel would be required before the storage test was started. As the storage was to be run at -134°C (250°R), it was decided to raise the temperature of the gel to -134°C (250°R) and observe its properties before the additional trimethylamine was added.

The gel was warmed to -134°C (250°R) and vigorously stirred and sparged with He to ensure that no appreciable amount of methane was present. During this process, the quantity of gel was reduced to 670 cc which was the amount required for the storage test. The settling rate of the gel was 40 cc in 1 hr.

The gel was cooled to the normal boiling point of methane, methane was added until the volume was 2100 cc and the trimethylamine addition resumed. An additional 69 gm of trimethylamine was injected into the mixture of diborane-methane-trimethylamino-borane particles. Upon completion of the trimethylamine addition, an additional 260 cc of diborane was added to the mixture to replace any diborane which could have been lost by evaporation during the trimethylamine addition. The gel was then sparged with He and intermittently stirred while it was warmed to -134°C (250°R).

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

The settling rate of the particles in the gelled diborane at -134°C (250°R) was 20 cc in 1 hr. As this rate appeared to be excessive, it was decided to hold the gel in the gelling vessel for a few days and observe its behavior before transferring it to the storage vessel. The results of the storage test in the gelling vessel are presented in Table XIV.

Upon completion of the storage test, the sample was vigorously stirred and the settling rate measured. The exudate volume was 200 cc after 1 hr. This compares with an exudate volume of 20 cc after 1 hr at the beginning of the storage test. This increase in settling rate indicates that particle growth had occurred.

TABLE XIV

STORAGE TEST OF GELLED DIBORANE

			Gelling Agent Concentrations, 25 wt%; 17 vol%		
Time hr:min	Temperature °C	Temperature °R	Gel Volume cc	Exudate Volume cc	Total Volume cc
0	-134	250	750	---	750
1	-134	250	730	20	750
6:20	-134	250	500	220	720
17:20	-134	250	400	280	680
29:35	-134	250	350	280	630
41:35	-134	250	350	270	620
53:35	-134	250	350	250	600
65:20	-134	250	350 or less*	240	590
77:20	-134	250	350 or less	200	550
89:00	-134	250	350 or less	175	525

*From this time on, the gel appeared to have a convex surface. It was not possible to observe the depth of this surface depression.

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

Experiment 79 - Discussion of Results

The results of the storage test at -134°C (250°R) indicate that particle growth, causing gel structure degradation, is occurring. The results of a test done during the last supplement of this contract had shown that the gel possessed excellent stability at -156°C (210°R) for a period of 12 days. Unfortunately, this test was terminated on the thirteenth day because of mechanical failure of the temperature control equipment. The gel prepared for Experiment 79 did not appear to be of as high a quality as the gel prepared for the previous experiment. This is shown by the fact that in this experiment 30 cc settling was observed in 15 hr at -156°C (210°R). In the earlier experiment the maximum settling rate that could have occurred was 1.4 cc/day.

Two probable explanations for the apparent lack of quality of the gel prepared in Experiment 79 are (1) the gelant concentration was lower than planned, and (2) the particles prepared are slightly larger than those previously prepared. Either probability could account for the apparent lack of quality. The concentration of the gelant is uncertain during the course of the experiment, especially if difficulty is experienced in maintaining the liquid methane level. In addition, a new injection tube was used which could well have an effect on the size of the particles prepared.

As was previously discussed, the data available indicate that particle growth occurred during the course of the experiment and the particle growth phenomenon is highly temperature dependent. Two probable explanations for the particle growth are (1) the gelant, trimethylaminoborane is slightly soluble in diborane, and (2) an exchange reaction is occurring between the BH_3 portion of the gelant molecule and the diborane. Either probability could account for particle growth and could be expected to be temperature dependent.

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

Consequently, the next experiment was designed to determine at what temperature particle growth becomes a significant factor. In addition, the injection tube was returned to the configuration used earlier and the difficulty with methane make-up during the trimethylamine addition needed to be resolved. This was done in order that the quality of the gel prepared would be similar to that of the earlier gel. Also, the effect of gelant concentration on the gel's storage properties was to be evaluated. It may well be possible, by increasing the gelant concentration to a higher level, to prepare a gel that would be stable at -134°C (250°R).

Particles that grow in a solution will, in almost all cases, reach a certain size, and no further growth will occur. Therefore, if the final "normal" size of trimethylaminoborane particles is small enough, it is possible that the particles would still possess gelling ability. Therefore, if the concentration of gelant is high enough, it may still be possible to prepare a stable, gelled diborane even though the gelant particle does grow in the diborane. This approach of using high gelant loadings is feasible because trimethylaminoborane is an excellent rocket fuel in its own right. The standard I_{sp} of pure trimethylaminoborane with OF_2 is 354 sec at a mixture ratio of 3.62. This is only 18 sec lower than the standard performance of OF_2/B_2H_6. Consequently, if a 40% gelant concentration is required, performance degradation would still be less than 2%.

The experimental work that determined the effect of equipment variables on particle size, the effect of gelant concentration and temperature on diborane gelled with trimethylaminoborane is reported below.

Experiment 84

As discussed above, the gelled B_2H_6 prepared in Experiment 79 did not appear to be of as high a quality as the gel prepared for the storage

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

test which was completed during the previous supplement to this contract. Consequently, this experiment was designed to duplicate the conditions used earlier.

> Twelve-hundred cc of liquid methane was added to the gelling vessel and 16.4 gm of B_2H_6 was dissolved in the methane. The solution was vigorously stirred and the volume brought up to 2100 cc by adding additional methane. The injection of the mixture of 50 volumes helium to 1 volume of trimethylamine was initiated and 38.7 gm of trimethylamine was added to the solution. The quantity of trimethylamine added was less than the amount planned because the injection tube clogged. Therefore, only 500 cc of gelled B_2H_6 was prepared rather than the 750 cc originally planned. The gelled B_2H_6 was prepared by adding B_2H_6 to the methane-particle mixture and then sparging off the methane. Because of the relatively small quantity of gel available, the gel cored during the attempt to transfer it to the storage vessel. Therefore, no storage data were obtained.

The gelled B_2H_6 that had been prepared contained 13.5 wt% gelling agent and appeared to be of excellent quality and its appearance was similar to the material prepared during the previous supplement to this contract.

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

Experiment 85

The experimental procedure was as described above. In this experiment the planned quantity of trimethylamine, 86.5 gm, was added to the diborane-methane solution. The particles gelled methane. Next, 765 cc of B_2H_6 was added to the mixture and the methane was sparged off with a stream of helium. During the sparging, the sample was stirred intermittently.

The extremely thick, gelled diborane (375 cc) was transferred from the gelling vessel to the storage vessel. Gelant concentration was 13.7 wt%.

During the first 24 hr of storage, at -156°C (210°R), no gel degradation occurred. Then, difficulty was experienced with the system temperature controller and two temperature excursions to -129°C (260°R) occurred during the next 48 hr. In both cases, the gel degraded and an exudate formed. During these temperature excursions 50 cc of diborane was lost by evaporation, an exudate formed, and the gel level decreased to 305 cc. The rapid degradation of the gel when exposed to elevated temperatures even for a short time showed that the particles of trimethylaminoborane grow rapidly when the temperature increases.

The temperature controller was modified and the difficulty with maintaining temperature corrected.

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

Therefore, it was decided to continue the experiment to determine if the settling stopped at any gelant concentration. The results are presented in Table XV.

A review of the data shows that, for the first 60 hr after the last temperature excursion, the gel level decreased at the relatively rapid rate of 1.2 cc/hr. The gelant particles apparently then reached an equilibrium and the settling rate decreased to a rate of 0.17 cc/hr. The most probable cause of the slow and continuous settling of the gelant particles is the particle growth that occurred during the two temperature excursions that occurred early in the experiment.

It was decided to investigate the stability of gelled diborane to determine if the gel was stable at -156°C (210°R) and, if the gel was stable at this temperature, to determine the temperature at which gel instability occurred.

Experiment 87

Twelve-hundred cc of liquid methane was added to the gelling vessel and 16.4 gm of B_2H_6 was dissolved in the methane. The solution was vigorously stirred and the volume brought up to 2100 cc by adding additional methane. Trimethylamine vapor (86.5 gm) diluted with He was injected into the diborane-methane solution. The particles of trimethylamino-borane thus prepared gelled methane. Next, 736 cc of B_2H_6 was added to the mixture and the methane was sparged off with a stream of helium. A portion (170 cc) of the extremely thick, gelled diborane

TABLE XV

STORAGE PROPERTIES OF GELLED B_2H_6 AT -156°C (210°R)

Gelant: Trimethylaminoborane

Time hr*	Gel Volume cc	Exudate cc	Total Volume cc
0.0	305	25	330
1.5	290	40	330
2.8	290	40	330
5.0	285	40	325
11.3	275	50	325
23.5	275	50	325
31.5	265	60	325
38.0	245	80	325
46.3	240	85	325
52.6	240	85	325
61.3	230	95	325
71.3	225 to 230	95	325
78.0	225 to 230	93	322
85.5	225 to 230	93	322
93.5	225 to 230	93	322
102.3	225 to 230	93	322
108.3	225 to 230	90	320
118.9	220	100	320
126.1	220	100	320
133.1	215	105	320
142.1	215	105	320
150.4	215	100	315
157.0	215	100	315
166.8	210 to 215	105	315
174.2	210 to 215	105	315
181.3	210 to 215	105	315
190.7	210 to 125	105	315
199.4	210	105	315
204.6	205	110	315
213.9	200	115	315
223.2	200	115	315
228.6	200	115	315
238.6	195 to 200	115	315
Experiment Terminated			

*Start: Fourth day of test after two temperature excursions to -129°C (260°R).

III, 1, Task XVII--Physical Characterization of Gelled OF_2 and B_2H_6 (cont.)

was transferred from the mix vessel to the storage vessel and the storage test started. The results of the test are presented in Table XVI.

The gel was stable for 18 days at -156°C (210°R) and then significant degradation of the gel structure became apparent. The results of the storage test demonstrated that diborane gelled with particles of trimethylaminoborane is not sufficiently stable to meet the 30-day storage goal which simulates the expected use-requirements. Consequently, it was recommended that work with trimethylaminoborane be terminated.

The next candidate gelling agent evaluated was trimethylamino-boron trifluoride. The experimental work which was discussed earlier led to the preparation of gelled B_2H_6 which met the objectives of this program.

TABLE XVI

EXPERIMENT 87
STORAGE PROPERTIES OF GELLED B_2H_6 AT -156°C (210°R)

Gelant: Trimethylaminoborane
Gelant Concentration: 14 wt%

Time days	Gel Volume cc	Exudate cc	Total Volume cc	
1	165	0	165	
2	165	0	165	
3	165	0	165	
4	165	0	165	
5	165	0	165	
6	165	0	165	
7	165	0	165	
8	165	0	165	
9	165	0	165	
10	165	0	165	
11	165	0	165	
12	165	0	165	
13	165	0	165	
14	165	0	165	
15	165	0	165	
16	165	0	165	
17	165	0	165	
18	165	0	165	Surface of the gel sample appears murky.
19	135	25	165	
20	120	45	165	

Test Terminated.

III, Technical Discussion (cont.)

2. TASK XVIII--CORRELATION OF APPARENT VISCOSITY AND GEL STRUCTURE

The gelation of a liquid imparts the properties of a semi-solid to the liquid when the liquid is at rest. These solid-like properties are responsible for the advantages of positional stability in a zero-g environment and reduced sloshing offered by gelled propellants. Consequently, to evaluate the degree of structure or semi-solid like properties possessed by a gel, it is desirable to have a technique for measuring the structure of gelled liquids. The most commonly used type of measurement for assessing the degree of structure possessed by a gel is a measurement of its resistance to deformation.

Over the course of the first two supplemental contracts, two methods of measuring the structure of the gels have been developed and used. The first employed a series of glass spheres of constant dia containing varying amounts of mercury to provide a range of weight. All the spheres were heavy enough to sink beneath the surface of the neat liquids but some of them were light enough to be supported by the surface of the gelled liquid. This technique for measuring the degree of structure was particularly suited for work with extremely reactive cryogenic propellants such as OF_2, because manipulation of the propellant is held to a minimum. The maximum weight which can be supported by the surface of the gel and the projected areas of the sphere are used to calculate the maximum force per unit area that can be supported by the surface. The value obtained in this manner is referred to as the structure index. It must be noted that this technique does not provide an absolute measurement of gel structure. However, the values obtained are an excellent measure of gel structure and show changes in the quantity of gel structure with changing gelling agent concentration. While the procedures described above were satisfactory when used with OF_2, it presented serious manipulation problems when used with reactive, air sensitive, highly toxic propellants. Consequently a second procedure was developed.

III, 2, Task XVIII--Correlation of Apparent Viscosity and Gel Structure (cont.)

The second procedure for measuring the structure of cryogenic gels was titled the Rising Platform Procedure. A thin metal disc is deeply immersed in the gel in a horizontal position, during the final mixing of the gel. This disc is then very slowly withdrawn from the gel; an inverted cone of propellant remains on the disc. The angle of repose, i.e., the angle between the horizontal disc and the side of the cone, is related to the degree of structure of the gel. The greater degree of structure, the greater the angle of repose. The angle of repose does not have to be measured directly because the mass of propellant which remains on the disc is an indirect measure of the angle of repose, i.e., as the degree of gel structure increases, the mass of propellant remaining on the disc increases. This mass, in turn, provides a direct measurement of the gel structure under zero shear conditions. As the measurement is made by a strain gage which is positioned external to the propellant-containing flask and connected to the rising platform by a wire, this method required only a small opening in the flask containing the propellant. It was, therefore, possible to avoid exposing the propellant to air by maintaining a helium sweep across the opening. In practice, it was found that this method did not yield highly reproducible results because it was difficult to prevent the connection from the rising platform to the strain gage from binding in its guide and because the mass of the plate and wire connecting the plate to the strain gage was large in relationship to the quantity being measured. Therefore, at the start of this portion of this study no completely satisfactory method for measuring the degree of structure of a gel was available. Consequently, most descriptions regarding the quality of the gels prepared are qualitative in nature and are based on visual observation.

A review of the flow data shows that, under flow conditions, the OF_2 and B_2H_6 gels flow in a manner similar to that of the neat liquids. This is especially apparent at higher shear rates where the slope of the characteristic flow curves is similar to that of water, a Newtonian liquid; see

III, 2, Task XVIII--Correlation of Apparent Viscosity and Gel Structure (cont.)

Figures 4, 9, and 10. Yet it is also apparent that the gels possess considerable structure when at rest. This is illustrated by the fact that OF_2 gels were stable for 30 days at 1 g even though the density of OF_2 is 1.776 gm/cc and gelant density is estimated to be at least 2.5 gm/cc under the test conditions. If the OF_2 gel did not possess structure, particulate settling would have been immediate. In the case of the diborane gels, the fact that the gels possessed structure when at rest is apparent because He bubbles remained suspended in the gel for the entire period of the storage test and showed no evidence of rising. Further evidence of the degree of structure is that it required a pressure of 1.5 psi to initiate the flow of the gelled B_2H_6 containing 12 wt% $(CH_3)_3N{\cdot}BF_3$ gelant. After flow was initiated, this gel at a 3.1-psi pressure drop exhibited a resistance to flow which was comparable to water under the same flow rate, or shearing conditions. Apparently, the gels maintain their structure until the shear force applied to them exceeds a certain limit. When this limit is exceeded, the loss of structure is extremely rapid and the gel behaves as a neat liquid. The available evidence indicates that the transition zone where the gel properties are intermediate between that of a liquid and that of a pseudo-solid covers a very short range of shear rates. Therefore, any description of the properties of these gels will exhibit a discontinuity, i.e., one set of properties are exhibited when the gel is at rest and a second set when it is being exposed to shearing forces which exceed the limiting value required to initiate flow.

The conclusions drawn from the above discussion and the flow data are that as the structure of the gelled OF_2 and gelled B_2H_6 increased, the apparent viscosity of the gel increased at a particular flow rate. However, because of the extreme shear-thinning that occurs when the gels are being flowed, no quantitative correlation could be developed. The data available indicate that a flow measurement will not give a useful indication of the degree of gel structure unless the measurement is made at extremely low shear

III, 2, Task XVIII--Correlation of Apparent Viscosity and Gel Structure (cont.)

rates. When experimental conditions are considered, it is apparent that flow measurements at extremely low shear rates would present many experimental problems. Consequently, it was apparent that it would be necessary to develop a new technique for measuring the degree of structure possessed by a gel at rest.

The development of the new procedure for assessing the structure of a gel was based on the following criteria:

(1) The method and required equipment should be usable at any temperature from -259 to 200°C.

(2) To eliminate the effect of shear thinning which changes the nature of the gel, the method should measure the resistance to flow or deformation, i.e., structure, possessed by the gel, without having the shearing force which is applied to the gel having a shear rate component.

(3) The method developed must not require any manual manipulation so that it can be safely used with toxic, air-sensitive propellants.

The equipment and procedures developed and some results obtained with them are described below.

Because it is necessary to eliminate the effect of shear thinning which changes the nature of the gel while measuring the resistance of the gel to deformation, it is necessary to apply a shearing force to the gel that does not contain a shear rate component. The device selected for applying this force is an electromagnet which would generate a magnetic field which would attract a soft iron rod. This device was selected because: (1) it is capable of operating over extremely wide temperature ranges; and (2) the rod would not

III, 2, Task XVIII--Correlation of Apparent Viscosity and Gel Structure (cont.)

move; therefore, no shear rate would be applied to the gel until the magnetic field generated by the electromagnet was strong enough to overcome the resistance of the gel to deformation.

A breadboard model of the proposed electromagnetic rheometer was constructed and used to evaluate the instrument. This breadboard model consisted of a hollow core electromagnet, a soft iron rod which has a flat plate located near the lower end, a beaker for holding the gel, a powerstat for controlling the power to the electromagnet, and a voltmeter for measuring the amount of power being supplied to the electromagnet. Figure 11 shows the equipment used.

The procedure for measuring the gel structure is as follows: The beaker was filled with gel and the rod and plate pushed into the gel. The electromagnet was then energized in small, stepwise increments until the rod was pulled out of the gel. The voltage required to create a magnetic field just strong enough to pull the rod from the gel was then read off the voltmeter. The instrument was calibrated by measuring the voltage required to move the rod in an empty container and to move the rod when the gel container was filled with the ungelled liquid. The results were calculated in the following manner:

$$\text{Gel structure} = \frac{V_g - [V_\varepsilon + (V_n - V_\varepsilon)]}{\text{Area of plate}} \times f$$

$$f = \frac{\text{wt of rod and plate, gm} \times 980.7}{V_e}$$

where: V_g = volts required to move the rod and plate in the gel

V_ε = volts required to move the rod in the empty gel container

V_n = volts required to move the rod in the gel container filled with the neat liquid

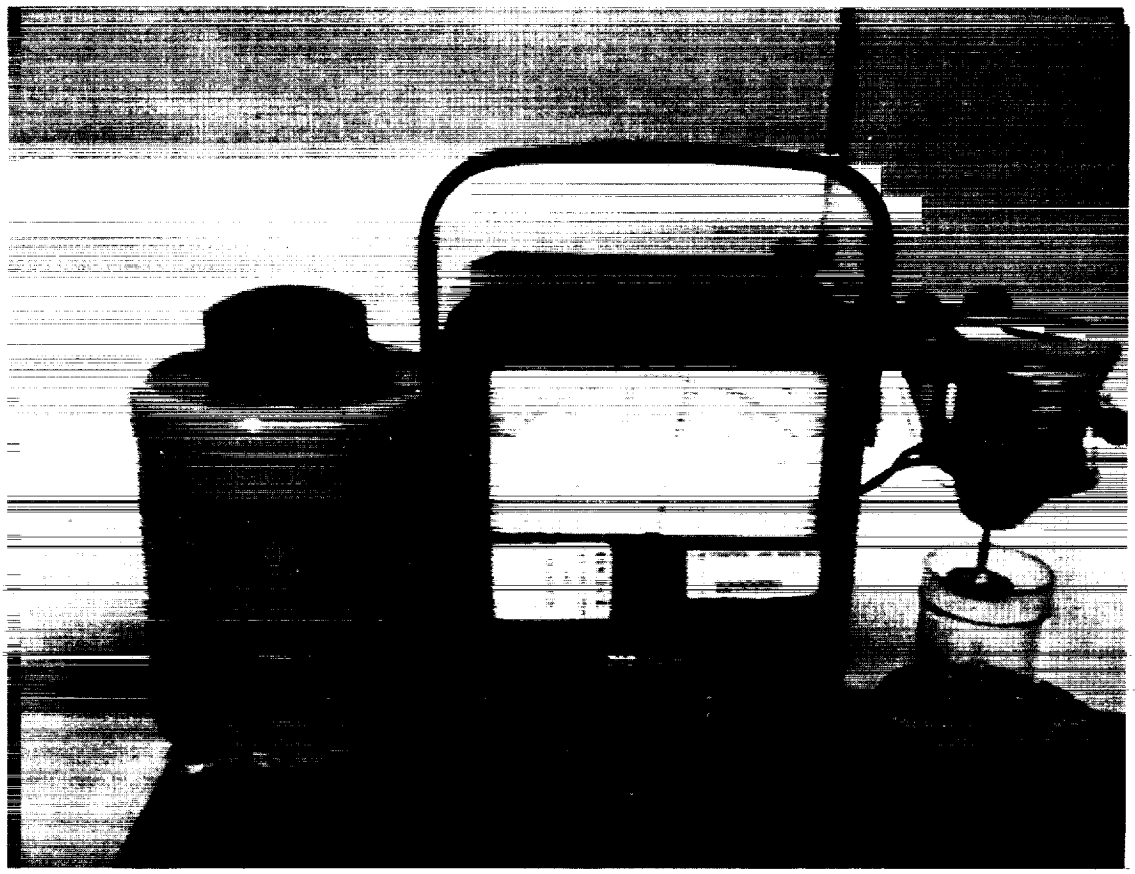

Figure 11. Breadboard Model of Electromagnetic Rheometer

III, 2, Task XVIII--Correlation of Apparent Viscosity and Gel Structure (cont.)

Table XVII presents some results obtained with a breadboard model of the electromagnetic rheometer.

TABLE XVII

GEL STRUCTURE MEASUREMENTS WITH AN ELECTROMAGNETIC RHEOMETER

Condition	Reading* volts	Gel Structure dynes/cm^2
Empty	38.5	----
Water	39.0	50
Water-Gel	55.3	1650
OB Oil**	44.6	600
Neat Oil	39.5	100
Oil Gel (thin)	42.2	350
Oil Gel (thick)	53.1	1400
Oil Gel (thickest)	85.6	4550

*Mean of three measurements, maximum deviation $\pm$ 0.5 volts.
**Viscosity of Oil 21,280 centipoise at 25°C.

Table XVIII compares the results obtained with a series of water gels with the rising sphere rheometer and the breadboard electromagnetic rheometer.

III, 2, Task XVIII--Correlation of Apparent Viscosity and Gel Structure (cont.)

TABLE XVIII

COMPARISON OF STRUCTURE INDEX MEASUREMENTS - RISING SPHERE RHEOMETER AND ELECTROMAGNETIC RHEOMETER

Sample Gelled Water	Rising Sphere Rheometer dynes/cm^2	Electromagnetic Rheometer dynes/cm^2
A	1900	2050
B	1750	1900
C	1500	1550
D	1100	950
E	2500	2550

Note that these values do not provide an absolute measure of the structure of a gel. However, the procedure is able to discriminate between gels of varying structure and the results should offer a useful guide. It is expected that the equipment used for actually measuring the structure of a cryogenic gel would consist of two hollow core electromagnets, an operation magnet, and a return magnet. A glass tube projects through the two hollow cores and is fitted with appropriate openings for adding the gel, expelling the gel, and washing out gel residues with an appropriate liquid. In addition, the tube is fitted with a stop. Inside the glass tube is a soft iron rod which has a flat plate located near the lower end. At the upper end of the glass tube is a signaling device to indicate when the inner rod has reached the limit of its upper travel. Figure 12 is a schematic diagram of the proposed electromagnetic rheometer.

The procedure for measuring the structure of a gel is as follows: The tube is filled with gel and the return electromagnet energized to pull the inner rod down to the stop. The magnet is then turned off. The upper magnet

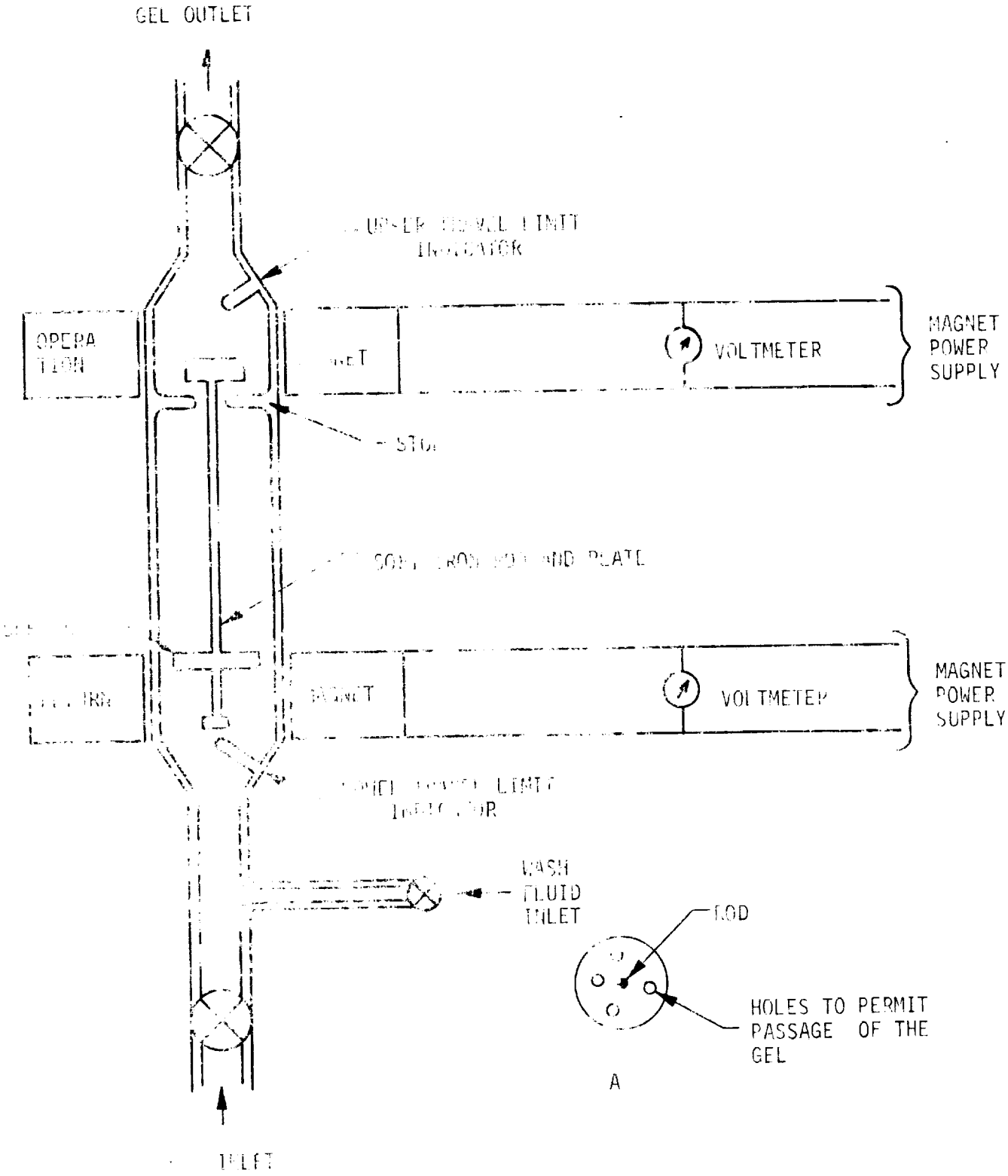

Figure 12. Proposed Electromagnetic Rheometer

III, 2, Task XVIII--Correlation of Apparent Viscosity and Gel Structure (cont.)

is then energized in small step-wise increments until the magnetic field is just strong enough to start the soft iron rod moving through the gel. The voltage required to start the iron rod moving through the gel less the voltage required to start the rod moving through the neat liquid (this quantity would be measured during the calibration runs) is a measure of the gel's resistance to deformation, i.e., the structure of the gel.

The proposed equipment and procedure for measuring the gel offers the following advantages: (1) except for the soft iron rod the equipment contains no moving parts; (2) the electromagnets which move the iron rod are not affected by cryogenic temperature and, therefore, the equipment can be used over a wide range of temperatures; (3) the measurement requires no manual manipulation of the equipment or reagent and, therefore, is useful with all types of gelled propellants; and (4) the shearing force applied to the gel does not contain a shear rate component because the rod does not move until the magnetic field exceeds a certain level. Once the rod starts to move, it will continue to move because it approaches the center of the magnetic field and the strength of a magnetic field varies inversely with the square of the distance from the center of the field.

3. TASK XIX--EXPULSION CHARACTERISTICS OF GELLED OF_2 AND B_2H_6

a. Expulsion Characteristics of OF_2 GELLED WITH $ClF_3 \cdot BF_3$

During the course of the flow measurements, the behavior of the gel in regard to hangup and coring was observed. There was no evidence of gel coring at any driving pressure or at any gelant concentration. The walls drained clean as the gel level decreased. Consequently, it is concluded that propellant acquisition and utilization will not be hampered by gelation.

III,3, Task XIX--Expulsion Characteristics of Gelled OF_2 and B_2H_6 (cont.)

b. Expulsion Characteristics of B_2H_6 Gelled with $(CH_3)_3N{\cdot}BF_3$

During the course of the flow measurements, the behavior of the gel in regard to hangup and coring was observed. There was no evidence of gel coring at any driving pressure or at any gelant concentration. The walls drained clean as the gel level decreased. Consequently, it is concluded that propellant acquisition and utilization will not be hampered by gelation.

c. Tankage and Outlet Configuration

In earlier work on this contract (Reference 1) it was determined that to obtain high expulsion efficiencies (ca. 98%) it appeared that a conical gel tank end-closure and outlet with an included angle of 90° or less is required if the acceleration level is 1 g. Other expulsion experience had shown that gel expulsion efficiency is dependent upon the acceleration level. Therefore, a narrower cone angle and steeper cone will probably be required for accelerations of less than 1 g. In addition, it was noted that any vibration increased expulsion efficiency. It is presumed that vibration helped to break the gel's adhesion to the tank wall, overcoming the gel's yield stress, and thus increasing shear forces on the gel have the effect of lowering the gel's apparent viscosity.

As the flow measurements on the gelled OF_2 and gelled B_2H_6 have demonstrated that these materials shear-thin very rapidly, it is expected that the vibrations occurring during an engine firing would probably eliminate any expulsion problems that might occur.

Over the course of this program it has been noted that coring problems do not occur if the outlet of the gelling vessel is in the form of an inverted J. If a direct outlet from the gelled propellant tank is used, it may be necessary to baffle the outlet.

III, Technical Discussion (cont.)

4. ADDITIONAL TECHNICAL EFFORT

a. Flow Behavior of Particulate Gels

Because flow in rocket system lines and injectors is almost always in the turbulent region, the experimental flow work reported in Section III,1,a,(3) and III,1,b,(3) was directed toward measuring the flow properties of the gels in the turbulent region. However, because of the nature of the gels under shearing conditions, it is difficult to determine at what flow rate the transition between laminar and turbulent flow occurs.

When the transition between laminar and turbulent flow occurs with a Newtonian liquid, the characteristic flow curve of the liquid will display a change in slope. This is because, in the laminar region, the readiness with which a fluid flows, i.e., the absolute viscosity* is a constant at any shear stress and shear rate and, therefore, the slope of the characteristic flow curve is constant. However, when flow becomes turbulent the resistance to flow is affected not only by the viscosity of the liquid but by the roughness of the pipe as compared to the diameter of the pipe. Thus, a change occurs in the slope of the characteristic flow curve.

The nature of flow in a pipe, laminar or turbulent, is dependent on the pipe diameter, the density and viscosity of the fluid, and the velocity

*For the purposes of this discussion, absolute viscosity is defined as the ratio of shear stress divided by shear rate and is a constant as long as flow remains laminar.
For the purposes of this discussion, apparent viscosity is defined as the ratio of shear stress divided by shear rate if the value obtained varies with changing shear rate.

III, 4, Additional Technical Effort (cont.)

of flow. The numerical value of these variables, known as the Reynolds number, is used to determine, without measurement, whether flow is laminar or turbulent. The Reynolds number is:

$$R = \frac{DvP}{N}$$

where D is diameter, v is velocity, P is density, and N is viscosity.

With Newtonian fluids, flow is usually considered laminar if the Reynolds number is less than 2000 and turbulent if the Reynolds number is greater than 4000. Between these two values flow may be either laminar, turbulent, or in transition from one type of flow to another. Because with a Newtonian fluid all of the variables that affect the Reynolds number are fixed at any given set of flow conditions, the determination of whether flow is turbulent or laminar is straightforward.

The determination of whether a shear thinning gel is flowing in the laminar or turbulent region under a given set of flow conditions is considerably more complex than it is with a Newtonian fluid because the viscosity of the gel is not constant. The apparent viscosity calculated from the flow data is affected by three factors. The first of these factors is the shear thinning property of the gel, i.e., loss in apparent viscosity caused by the application of shearing forces to the gel. The second factor is the effect that gel structure will have on the thickness of the boundary layer where flow is always laminar. The third factor is the effect that turbulent flow, when the gel is flowing in the turbulent region, has on the apparent viscosity of the gel. Because of these variables, the absolute viscosity of the gel cannot be calculated and, therefore, a valid Reynolds number cannot be calculated.

III, 4, Additional Technical Effort (cont.)

The best available guide for determining whether a shear thinning gel is flowing in the laminar or turbulent region is the characteristic flow curve. In the shear rate region where the characteristic flow curve has a horizontal orientation and shear thinning is the predominant phenomenon occurring within the gel, flow is probably laminar. As the shape of curve inclines towards the vertical, flow is probably in the transition zone. When the shape of the characteristic flow curve of a gel approaches the vertical and is similar to that of a Newtonian liquid flowing in the turbulent region, flow is almost certainly turbulent.

In the case of the gelled OF_2 flow measurements, reported in Section III,1,a,(3), flow is probably turbulent at all shear rates above 1000 sec^{-1}.

In the case of the gelled B_2H_6 flow measurements, reported in Section III,1,b,(3), flow of the 9.5 wt% gel is probably turbulent at all shear rates above 1100 sec^{-1}. The flow of the 12 wt% gel probably does not become turbulent until the shear rate reaches 1700 or 1800 sec^{-1}.

b. Theoretical Performance of the Gelled OF_2/Gelled B_2H_6 Combination

The calculated specific impulse of the neat OF_2/B_2H_6 propellant is 372 sec (1000/14.7) and the calculated specific impulse of 94% OF_2-6% $ClF_3 \cdot BF_3/B_2H_6$ is 363 sec (1000/14.7). Therefore, the specific impulse penalty caused by the gelation of OF_2 with $ClF_3 \cdot BF_3$ is only 2.5%. The calculated specific impulse of OF_2/93% B_2H_6-7% $(CH_3)_3N \cdot BF_3$ is 369 sec (1000/14.7). Therefore, the performance penalty caused by the gelation of diborane is only 0.8%. The calculated specific impulse of the gelled OF_2/gelled B_2H_6 bipropellant system with the OF_2 gelled with 6 wt% $ClF_3 \cdot BF_3$ and the B_2H_6 gelled with 7 wt% $(CH_3)_3N \cdot BF_3$ is 360 sec (1000/14.7); the specific impulse penalty incurred by the gelant concentrations required for both propellants is 3.2%.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

1. CONCLUSIONS

The conclusions which are drawn from this research program are:

a. A simple and practical synthesis technique for the preparation of micron-size particles of $ClF_3 \cdot BF_3$ has been developed and reduced to a routine operation.

b. Excellent gels of OF_2 have been prepared using $ClF_3 \cdot BF_3$ particles. The gels have been stored for 30 days without any evidence of gel degradation and the flow properties of the gels are similar to that of water.

c. The volatility of $ClF_3 \cdot BF_3$ at 25°C was conclusively demonstrated.

d. Bromine pentafluoride, bromine trifluoride, and boron trifluoride particles do not gel liquid OF_2 at acceptable concentrations.

e. A simple and practical synthesis technique for the preparation of micron-size particles of $(CH_3)_3N \cdot BF_3$ has been developed and reduced to a routine operation.

f. Excellent gels of B_2H_6 have been prepared using $(CH_3)_3N \cdot BF_3$ particles. The gels have been stored for 30 days without any evidence of gel degradation and the flow properties of the gels are similar to that of water.

g. The volatility of $(CH_3)_3N \cdot BF_3$ under the conditions that would exist in a rocket engine at shutdown was conclusively demonstrated.

IV, 1, Conclusions (cont.)

h. Diborane gelled with trimethylaminoborane does not meet the storage stability requirements of this program.

i. No useful correlation was found between the flow properties of gelled oxygen difluoride and gelled diborane and gel structure. A novel procedure for measuring without manual manipulation the structure of particulate gels was developed.

j. No evidence of gel coring or gel hangup was observed and it is concluded that propellant acquisition and utilization will not be hampered by gelation.

2. RECOMMENDATIONS

a. The performance of gelled oxygen difluoride and gelled diborane should be evaluated at the 100 lb thrust level, and long-term storage tests (6 to 12 months) should be started.

b. Concurrently with the performance tests, propellant acquisition techniques and overall gel behavior should be further evaluated.

SECTION V

PROGRAM PERSONNEL

The NASA Project Manager for this program was Mr. J. Suddreth, NASA Headquarters, OART; the NASA Technical Manager was Mr. D. L. Young of the Jet Propulsion Laboratory.

The Aerojet Program Manager and Project Engineer was Mr. R. H. Globus. The diborane and oxygen difluoride gel formulation and testing studies were performed under the direction of Mr. Globus with the assistance of Mr. J. A. Cabeal. Drs. S. D. Rosenberg and E. M. Vander Wall acted as consultants during this program.

REFERENCES

1. System Analysis of Gelled Space-Storable Propellants, Aerojet-General Corporation, Contract NAS 7-473, Report 1038-011R, Volume 1, May 1967.

2. System Analysis of Gelled Space-Storable Propellants, Aerojet-General Corporation, Contract NAS 7-473, SA-1, Report 1038-02S, Summary Report, July 1968.